Nonequilibrium steady-state picture of photosynthetic light harvesting

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We formulate a comprehensive theoretical description of excitation harvesting in molecular aggregates that mimics photosynthetic light harvesting under natural conditions. An efficient numerical scheme that respects the continuity equation for excitation fluxes is developed to compute the nonequilibrium steady state (NESS) arising from the interplay between excitation generation by weak incoherent radiation, excitation relaxation, dephasing, trapping at the load, and recombination. We conclude that the non-zero values of nonequilibrium stationary coherences do not influence the light-harvesting efficiency, which is ultimately determined solely by the diagonal elements (populations) in the so-called preferred basis of the NESS. In the limit of long trapping time, we find that the NESS is quite similar to the excited-state equilibrium, in which the stationary coherences originate from the excitation–environment entanglement. For shorter trapping times, we demonstrate how the properties of the NESS can be extracted from the time-dependent description of an incoherently driven, but unloaded aggregate. This relation between stationary and time-dependent pictures is valid provided that the trapping time is longer than the decay time of dynamic coherences accessible in femtosecond spectroscopy experiments. While neither the dynamic nor the stationary coherences are directly relevant for natural light harvesting, their imprints on the NESS may be identified.

I. INTRODUCTION

The observation of unexpectedly long-lived oscillatory features of ultrafast spectroscopic signals measured on photosynthetic pigment–protein complexes has generated much excitement during the last decade. The idea that (dynamic) coherences dominating these signals may be directly relevant to natural light harvesting, which is triggered by stationary incoherent sunlight, has been driving intense research activities in the field. Insights from ultrafast spectroscopies are indispensable in determining the underlying Hamiltonian of the system under investigation, from which the dynamics of excitation energy transfer (EET) under any excitation condition may be inferred (as long as the excitation is sufficiently weak). A number of experimental and theoretical studies speculating about a positive impact of coherences and entanglement on the biological EET are performed on the so-called unloaded systems. Such systems feature no transmission of photoinduced excitations to the reaction center (RC or load) from which the excitation energy is eventually harvested. Furthermore, the time scales addressed in these studies are generally much shorter than those representative of exciton recombination, either radiative or nonradiative. Direct experimental insights into the dynamics of molecular aggregates initiated by incoherent light are limited. Therefore, at present, the possible relevance of some sort of quantum coherence for EET under natural conditions is best examined within appropriate theoretical models.

Such models should contain a realistic description of photoexcitation by natural incoherent light, whose intensity is essentially constant from the molecular viewpoint. Thus, the physically plausible description of natural light harvesting should feature continuous generation of electronic excitations by light, their continuous delivery to the RC, and their continuous loss by recombination. The EET is then studied from the standpoint of nonequilibrium steady states (NESSs), which arise as a result of excitation photogeneration, phonon-induced relaxation, dephasing, trapping at the RC, and recombination. Furthermore, the coupling between the radiation and absorbing pigments is, in general, weak, so that its second-order treatment is reasonable. Then, the only information we need about the radiation is its first-order correlation function, which can be either modeled by appropriate expressions or obtained by a suitable ensemble average. Excitation and deexcitation events can be treated within the Born–Markov approximation by Lindblad dissipators or by establishing the Bloch–Redfield quantum master equation. Approaching the problem from the perspective of open quantum systems, one can introduce an appropriate spectral density of light–matter coupling and possibly treat it even beyond the second order.

Reasonable models of photosynthetic EET should not overlook the non-Markovian interplay between photoinduced electronic excitations and nuclear reorganization processes whose relevance is emphasized by ultrafast spectroscopic studies. To that end, a number of studies attempt to combine an explicit treatment of the photoexcitation step with a nonperturbative approach to the excitation–environment coupling. The method of choice for an exhaustive treatment of excitation–environment coupling are hierar-
chical equations of motion (HEOM). In the accompanying paper, we combine HEOM with a second-order treatment of light–matter coupling for light of arbitrary properties. Our method correctly captures light-induced reorganization processes and nonequilibrium evolution of the bath between the two interactions with light.

Recently, a number of groups have suggested that stationary coherences in the energy basis (interexciton coherences) or local basis (intersite coherences) under incoherent illumination may improve the light-harvesting efficiency in photosynthetic systems. However, the majority of existing theoretical approaches to NESSs in photosynthetic light harvesting typically feature a simplified treatment of the photoexcitation or a simplified treatment of excitation relaxation and dephasing. Also, efficient algorithms that avoid the explicit temporal propagation in the computation of NESSs induced by natural incoherent light have just begun to be developed. Therefore, there is still an urge to construct theoretical methods that circumvent the disparity between the time scales of EET dynamics and incoherent excitation sources, and yet meet the two requirements outlined in the above text.

Another pertaining issue is the origin of stationary coherences, i.e., whether they are primarily induced by incoherent radiation or by the coupling to the protein environment. The authors of Ref. argued that the NESS coherences ultimately stem from the entanglement of electronic excitations with the environment. This entanglement has been systematically studied both analytically and numerically within the undriven and unloaded spin–boson model. The two-level system displays noncanonical equilibrium statistics whose deviation from the canonical equilibrium statistics can be conveniently measured by a single parameter. This parameter can be interpreted as the angle by which the basis in which the system’s Hamiltonian (or the system–bath interaction Hamiltonian) is diagonal should be rotated to obtain the diagonal reduced density matrix (RDM). The basis in which the RDM is diagonal is thus singled out by the environment, and the corresponding basis states are known as the preferred (or pointer) states within the framework of the decoherence theory. The concept of preferred basis is useful whenever representation-dependent issues, such as the ones we are after in this study, arise.

In this paper, we extend the ideas developed in Ref. to examine the properties of the NESS that arises in an incoherently driven and loaded excitonic aggregate. Adapting the algorithm presented in Ref., we devise a procedure to find the NESS of our recently proposed HEOM that incorporates incoherent photoexcitation and to properly define light-harvesting efficiency under incoherent illumination. Our theoretical approach fully respects the continuity equation for excitation fluxes. We find that non-zero values of coherences in any basis neither enhance nor lower the efficiency, which is ultimately determined by the diagonal elements of the RDM in the so-called preferred basis of the NESS. While our theoretical method is quite general and applicable to arbitrary excitonic networks, we investigate the properties of the NESS using the appropriately parameterized model dimer. For realistic values of the load extraction time, we conclude that light-induced coherences are completely irrelevant in the NESS, which is then close to the noncanonical equilibrium of an undriven and unloaded system. We find that the NESS of a driven and loaded system is intimately related to the dynamics of a driven, but unloaded system, that takes place on the time scale of the excitation trapping at the load. This close connection between the dynamic and stationary picture is correct provided that the load extraction time is longer than the time scale of coherence dephasing, which is in principle accessible in ultrafast spectroscopies.

The paper is structured as follows: The model and method are presented in Secs. and respectively. In Sec. we discuss, on general grounds, the impact of stationary coherences in any basis on the light harvesting efficiency, and we set stage for our numerical investigations, whose results are presented in Sec. Section concludes the paper by summarizing its principal findings.

II. MINIMAL MODEL

We consider the simplest EET system, a molecular aggregate composed of two mutually coupled chromophores (a dimer, a spin–boson-like model). Although a similar model has been repeatedly used by many authors to gain insight into fundamentals of light harvesting under incoherent illumination, our analysis uses a rigorous theoretical approach to investigate in greater detail certain properties of the NESS that have not received enough attention so far. Electronic excitations of the model dimer are modeled within the Frenkel exciton model and the corresponding Hamiltonian reads as

\[
H_M = \sum_j \varepsilon_j |l_j⟩⟨l_j| + \sum_{jk} J_{jk} |l_j⟩⟨l_k|.
\]  

(1)

In Eq. |l_j⟩ is the singly excited state localized on chromophore j, \(\varepsilon_j\) is its vertical excitation energy, while \(J_{jk}\) are resonance couplings (we take \(J_{kk} = 0\)). We limit our discussion to the manifold of singly excited states, which is justified under the assumption that the driving by the radiation is sufficiently weak. The aggregate is in contact with the thermal bath, which represents its protein environment, and which is modeled as a collection of independent oscillators labelled by site index j and mode index ξ

\[
H_B = \sum_{jξ} \hbar \omega_ξ b_{jξ}^† b_{jξ}.
\]  

(2)

The phonon creation and annihilation operators \(b_{jξ}^†\) and \(b_{jξ}\) entering Eq. (2) satisfy Bose commutation relations.
The aggregate is driven by weak radiation and the generation of excitations is described in the dipole and rotating-wave approximations

\[ H_{M-R} = -\mu_{eg} \cdot \mathbf{E}^{(+)} - \mu_{ge} \cdot \mathbf{E}^{(-)}. \]  

(3)

In Eq. (3), operators \( \mathbf{E}^{(\pm)} \) are the positive- and negative-frequency part of the (time-independent) operator of the (transversal) electric field, while the \( eg \) part of the dipole-moment operator reads as

\[ \mu_{eg} = \mu_{ge}^\dagger = \sum_j |j\rangle \langle j| \langle g_j|. \]  

(4)

We assume that transition dipole moment \( \mathbf{d}_j \) of chromophore \( j \) does not depend on nuclear coordinates (Condon approximation). The interaction of photoinduced excitations with the environment is taken to be in Holstein form, i.e., it is local and linear in oscillator displacements

\[ H_{M-B} = \sum_j |j\rangle \langle j| \sum_\xi \gamma_{j\xi} (b^\dagger_{j\xi} + b_{j\xi}) \equiv \sum_j V_j u_j. \]  

(5)

We assume there are two possible channels through which photogenerated excitons may decay. The first one is their transfer to the charge-separated state in the RC, in which case they are usefully harvested. On the other hand, exciton recombination, either radiative or nonradiative, is detrimental to the efficiency of EET. While exciton recombination, either radiative or nonradiative, is detrimental to the efficiency of EET. While

\[ C(t) = \langle u_j(t) u_j(0) \rangle_B = \sum_{m=0}^{K-1} c_m e^{-\mu_m t} + 2\Delta \delta(t). \]  

(7)

In Eq. (7), the collective bath coordinate \( u_j \) is defined in Eq. (3), the expansion coefficients \( c_m \) may be complex, while the corresponding decay rates \( \mu_m \), as well as the white-noise-residue strength \( \Delta \), are assumed to be real and positive. The bath correlation function is usually expressed in terms of the environmental spectral density \( J(\omega) \) \( [\beta = (k_B T)^{-1}, \text{where } T \text{ is the temperature}] \)

\[ C(t) = \frac{\hbar}{\pi} \int_0^{+\infty} d\omega J(\omega) \frac{\Gamma_{\text{out}}}{e^{\beta \hbar \omega} - 1}. \]  

(8)

which conveniently combines information on the density of environmental-mode states and the respective coupling strengths to electronic excitations. \( \beta \) \( \left[ \text{Eq. (7)} \right] \) We explicitly treat only \( K = N_{BE} + N_f \) terms in Eq. (7), where \( N_{BE} \) and \( N_f \) are the numbers of explicitly treated poles of the Bose–Einstein function and the bath spectral density, respectively. We assume the environmental spectral density of the overdamped Brownian oscillator

\[ J(\omega) = \frac{2\lambda}{\omega^2 + \gamma^2}, \]  

(9)

where \( \lambda \) is the reorganization energy, while \( \gamma^{-1} \) is the characteristic time scale for the decay of the bath correlation function \( C(t) \).

The exponential decompositions embodied in Eqs. (4) and (7) enable us to formulate the problem as HEOM incorporating photoexcitation. As demonstrated in Ref. [53], the hierarchy consists of two parts, one in the \( eg \) sector, and another in the \( ee \) sector. Each density matrix \( \sigma_{nm}(t) \) is uniquely characterized by vector \( \mathbf{n} \) of non-negative integers \( n_{j,m} \), where index \( j \) enumerates chromophores, while index \( m \) counts terms in the decomposition of \( C(t) \) [Eq. (7)]. In order to describe excitation harvesting by the RC and recombination, we augment our formalism by effective Liouvillians describing these two processes. As demonstrated in Ref. [54], these Liouvillians appear on each level of HEOM. Performing the appropriate rescalings, which ensure that auxiliary density operators are all dimensionless and consistently smaller in deeper levels of the hierarchy, we obtain the following equations describing the NESS we are interested in

III. METHODS

We use our exact description of weak-light-induced exciton dynamics in molecular aggregates, which is developed in the accompanying paper. [53] The radiation correlation function, which is the only property of the radiation entering our reduced description, is modeled by the following expression:

\[ G^{(1)}(\tau) = \left\langle E^{(+)}(\tau) E^{(-)}(0) \right\rangle_R = I_0 \exp \left( i\omega_c \tau - \tau/\tau_c \right), \]  

(6)
$(\gamma_n = \sum_{j,m} n_{j,m} \mu_{nm})$

$$0 = -\frac{i}{\hbar \gamma} [H_M, \sigma_{ss}^{ee,n}] - \frac{\gamma_n}{\gamma} \sigma_{ss}^{ee,n}$$

$$+ \left( i \omega_c - (\tau_c \gamma)^{-1} \right) \sigma_{ss}^{ee,n} - \frac{\Delta}{\hbar^2 \gamma} \sum_j V_j \sigma_{ss}^{ee,n}$$

$$+ \delta_{n,0} \frac{i}{\hbar \gamma} \mu_{eg}$$

$$+ i \sum_{j=0}^{K-1} \sum_{m=0}^{j} \sqrt{1+n_{j,m}} \frac{c_m}{(\hbar \gamma)^2} V_j \sigma_{ss}^{ee,n}_{j,m}$$

$$0 = -\frac{i}{\hbar \gamma} [H_M, \sigma_{ss}^{ee,n}] - \frac{\gamma_n}{\gamma} \sigma_{ee,n}$$

$$- \frac{\Delta}{\hbar^2 \gamma} \sum_j V_j \sigma_{ss}^{ee,n}$$

$$+ \frac{i}{\hbar \gamma} \mu_{eg} \sigma_{ss}^{ee,n} + \frac{i}{\hbar \gamma} \sigma_{ss}^{ee,n} \mu_{eg}$$

$$+ \gamma^{-1} L_{\text{rec}}[\sigma_{ss}^{ee,n}] + \gamma^{-1} L_{\text{RC}}[\sigma_{ss}^{ee,n}]$$

$$+ i \sum_{j=0}^{K-1} \sum_{m=0}^{j} \sqrt{1+n_{j,m}} \frac{c_m}{(\hbar \gamma)^2} V_j \sigma_{ss}^{ee,n}_{j,m}$$

$$- i \sum_{j=0}^{K-1} \sum_{m=0}^{j} \sqrt{n_{j,m}} \frac{c_m}{(\hbar \gamma)^2} V_j \sigma_{ss}^{ee,n}_{j,m}.$$

In the NESS, the continuity equation for exciton currents should be valid, i.e., the number of generated excitons per unit time must balance the sum of the recombination and trapping exciton fluxes. This is physically clear, and it is seen from a more formal perspective by taking the trace (with respect to the electronic system of interest) of Eq. (11) in which $n = 0$. This results in

$$J_{\text{gen}} - J_{\text{RC}} - J_{\text{rec}} = 0. \quad (12)$$

In the continuity equation [Eq. (12)], we define all currents to be positive, while the sign is determined by the "direction" of the current (+/- if it leads to an increase/a decrease in the exciton number). In more detail, the definitions of currents, which are dimensionless in our description, are

$$J_{\text{gen}} = \frac{2}{\hbar \gamma} \text{Im} \text{Tr}_M \left\{ \sigma_{ss}^{ee,0} \mu_{eg}^\dagger \right\}, \quad (13)$$

$$J_{\text{RC}} = -\gamma^{-1} \text{Tr}_M \left\{ L_{\text{RC}} [\sigma_{ss}^{ee,0}] \right\}, \quad (14)$$

$$J_{\text{rec}} = -\gamma^{-1} \text{Tr}_M \left\{ L_{\text{rec}} [\sigma_{ss}^{ee,0}] \right\}. \quad (15)$$

Let us immediately note that currents $J_{\text{gen}}, J_{\text{RC}},$ and $J_{\text{rec}}$ are written in a basis-invariant manner. This feature is quite appealing, since one can express currents in terms of populations and coherences in any particular basis. The light-harvesting efficiency is defined as

$$\eta = \frac{J_{\text{RC}}}{J_{\text{gen}}}. \quad (16)$$

As discussed in the accompanying paper, for realistic values of the light coherence time $\tau_c \sim 1 \text{fs}$, the expression for the generation current may be further simplified to

$$J_{\text{gen}} = 2 \frac{I_0}{(\hbar \gamma)^2} \text{Tr}_M \left\{ \mu_{eg} |g\rangle \langle g| \mu_{ge} \right\}. \quad (17)$$

In other words, possible enhancements in $\eta$ due to coherences in any basis ultimately originate from the expression for the trapping Liouvillian $L_{\text{RC}}$, as detailed in the following section.

IV. DIFFERENT BASES

In the literature on the physics of photosynthetic light harvesting, two bases play special roles. The first one is basis $\{|l_j\rangle\}$ of singly excited states localized on single chromophores (local or site basis). While Hamiltonian parameters are usually known in the local basis, the description of, e.g., absorption properties of a photosynthetic aggregate is usually performed in the excitonic basis $\{|x_j\rangle\}$, i.e., in the basis of stationary states of the isolated-aggregate Hamiltonian $H_M$. Claims about possible impact of coherences on the efficiency of photosynthetic light harvesting are usually made with the coherences in the excitonic or local basis in mind.

Tomasi and Kassal have recently classified different types of possible coherent enhancements of light harvesting efficiency according to the basis in which the excitation decay mechanisms are defined. Let us now focus on the trapping at the RC. Two forms for the Liouvillian $L_{\text{RC}}[\rho]$ are widely used in the literature. If site $j_0$ is closest to the RC, so that it is essentially the sole site coupled to it, one uses the so-called localized-trapping Liouvillian

$$L_{\text{RC}}[\rho] = \tau_{\text{RC}}^{-1} \left( \langle \text{RC}|l_{j_0} \rho |l_{j_0}\rangle \langle l_{j_0}|l_{j_0}| \rho \right) - \frac{1}{2} \left\{ |l_{j_0}\rangle \langle l_{j_0}|, \rho \right\}. \quad (18)$$

where $\tau_{\text{RC}}$ is the characteristic time scale on which the populations are delivered from site $j_0$ to the RC. However, even in such a situation, the excitation transfer to the RC should be regarded as the multichromophoric Förster transfer, so that it is more appropriate to
employ the so-called delocalized-trapping Liouvillian.

\[
\mathcal{L}_{\text{RC}}^{\text{deloc}}[\rho] = \tau_{\text{RC}}^{-1} \sum_j |\langle x_j | l_j \rangle|^2 \\
\times \left( \langle \text{RC} | \langle x_j | \rho | x_j \rangle | \text{RC} | - \frac{1}{2} \{ | x_j \rangle \langle x_j |, \rho \} \right) .
\]

(19)

If we assume the trapping at the RC to be governed by Eq. (18), the trapping current \( J_{\text{RC}} \) in Eq. (14) depends only on site populations, and on both exciton populations and interexciton coherences. If, on the other hand, we assume that the trapping is governed by Eq. (19), \( J_{\text{RC}} \) is expressed in terms of exciton populations only, while its expression in the local basis contains both site populations and intersite coherences. This has been recognized in recent studies, which ascertain that possible coherent enhancements of the efficiency can be achieved only when the coherence occurs in a basis different from that in which the trapping or recombination are modeled.

We assume that the (nonradiative) recombination may occur from each site with the same rate constant \( \tau_{\text{rec}} \), and the appropriate Liouvillian reads as

\[
\mathcal{L}_{\text{rec}}[\rho] = \tau_{\text{rec}}^{-1} \sum_j \left( |g_j \rangle \langle l_j | \rho | l_j \rangle | g_j \rangle - \frac{1}{2} \{ | l_j \rangle \langle l_j |, \rho \} \right) .
\]

(20)

However, whatever the form of the effective trapping and recombination Liouvillians is, there will always be a basis in which \( J_{\text{RC}} \) is entirely expressed in terms of populations in that basis. Such a basis will be denoted as \( \{|p_j\rangle | j\} \) and termed the preferred basis of the NESS under investigation. The excited-state sector of the steady-state RDM \( \rho_{ee}^{ss} \) in the preferred basis reads as

\[
\rho_{ee}^{ss} \equiv \sigma_{ee,0}^{ss} = \sum_j p_j |p_j\rangle \langle p_j| .
\]

(21)

The preferred basis is determined by the competition between excitation generation, pure dephasing, energy relaxation, excitation trapping at the RC and recombination.

The excitonic (or site) basis and the preferred basis of the NESS are connected through a unitary transformation. For our model dimer, the most general transformation of that kind can be parameterized by four real parameters, so that the basis vectors in the preferred basis are expressed in terms of the basis vectors in the excitonic basis as follows

\[
\begin{pmatrix} |p_0\rangle \\ |p_1\rangle \end{pmatrix} = e^{i \phi_{px}/2} \begin{pmatrix} e^{i \psi_{px}} & 0 \\ 0 & e^{-i \psi_{px}} \end{pmatrix} \\
\times \begin{pmatrix} \cos \theta_{px} & \sin \theta_{px} \\ -\sin \theta_{px} & \cos \theta_{px} \end{pmatrix} \\
\times \begin{pmatrix} e^{i \Delta_{px}/2} & 0 \\ 0 & e^{-i \Delta_{px}/2} \end{pmatrix} \begin{pmatrix} |x_0\rangle \\ |x_1\rangle \end{pmatrix} .
\]

(22)

Due to the phase freedom, we can immediately remove parameters \( \psi_{px} \) and \( \phi_{px} \) from further discussion, so that we are left with only two parameters, \( \theta_{px} \) and \( \Delta_{px} \). From our subsequent discussion, it will emerge that the rotation angle \( \theta_{px} \) is closely related to the analogous rotation angle which measures the deviation from the noncanonical statistics in the undriven and unloaded system (no generation, trapping, and recombination). The phase \( \Delta_{px} \) is intimately connected to the rates of excitation trapping and recombination, which remove excitations from the system.

The parameters \( \theta_{px} \) and \( \Delta_{px} \) can be related to the Bloch angles \( \theta_B^x \) and \( \phi_B^x \) that are commonly used to characterize the basis in which the RDM is diagonal. Namely, one can always normalize \( \tilde{\rho}_{ee}^{ss} \) to obtain \( \rho_{ee}^{ss} \) whose trace is unity and whose eigenvalues will be denoted as \( \tilde{\rho}_\beta \). For the model dimer, the operator \( \tilde{\rho}_{ee}^{ss} \) can always be expressed as

\[
\tilde{\rho}_{ee}^{ss} = \frac{1}{2} (I + a \cdot \sigma) ,
\]

where \( I \) is the 2 \( \times \) 2 unity matrix, while \( \sigma = \{ \sigma_1, \sigma_2, \sigma_3 \} \) are three Pauli matrices. Let \( \sigma_3 \) be diagonal in the excitonic basis (i.e., \( \sigma_3 = |x_0\rangle \langle x_0| - |x_1\rangle \langle x_1| \)) and let \( a^x \) be the corresponding vector in Eq. (23). Then it can be shown that the spherical angles \( \theta_B^x \) and \( \phi_B^x \) on the Bloch sphere are related to parameters \( \theta_{px} \) and \( \Delta_{px} \) as follows

\[
\cos \theta_B^x = \frac{a_3}{|a^x|} = \text{sgn}(2 \tilde{\rho}_0 - 1) \cdot \cos(2 \theta_{px}) ,
\]

(24)

\[
\tan \phi_B^x = \frac{a_3}{a_1} = -\tan(2 \Delta_{px}) .
\]

(25)

Equations (24) and (25) relate \( \theta_{px} \) and \( \Delta_{px} \) to the Bloch angles \( \theta_B^x \) and \( \phi_B^x \) that are straightforwardly obtained from vector \( a^x \). In a similar manner, one obtains parameters \( \theta_{pl} \) and \( \Delta_{pl} \) of the unitary transformation that connects the preferred and the local basis. The rotation angle \( \theta_{px} \) can always be chosen in the range \((0, \pi/4)\), while \( \Delta_{px} \in (-\pi/4, \pi/4) \). This is discussed in greater detail in Sec. SI of the Supplementary Material.

V. NUMERICAL RESULTS

Numerical computations are performed on an asymmetric dimer, which is schematically presented in Fig. 1. The parameters of our model are summarized in Table I.
more elaborate treatment of excitation harvesting should explicitly consider both the forward and backward excitation transfer from the absorbing aggregate to the state of primary electron donor in the RC, as well as the primary charge separation, after which the excitation may be considered as usefully harvested. Previous theoretical works employing a simplified description of excitation harvesting, as we do here, typically assumed that $\tau_{RC}$ is of the order of picoseconds. On the other hand, experiments on various species of photosynthetic bacteria, as well as computational studies, suggest that the appropriate value of our parameter $\tau_{RC}$ may be as large as a couple of tens of picoseconds. The reported values of the reorganization energy in the FMO complex range from tens to hundreds of inverse centimeters. Having all these things considered, the values of $\tau_{RC}$ and $\lambda$ will be varied in wide, yet physically relevant ranges, in order to examine how they impact the properties of the NESS.

The NESS is obtained by solving coupled Eqs. (10) and (11) by adapting the algorithm that was introduced in Ref. 18. The computational approach of Ref. 18 was developed to compute the equilibrium RDM of an undriven and unloaded system and it relies on the Jacobi iterative procedure to solve a diagonally dominant system of linear algebraic equations. The procedure is repeated until a convergence criterion, which in Ref. 18 was related to the magnitude of the ADO elements, is satisfied. Here, we deal with a driven and loaded system, and our computations are terminated once the continuity equation [Eq. (12)] is satisfied with a desired numerical accuracy. More details on our numerical scheme to compute the NESS of a driven and loaded dimer can be found in Sec. SII of the Supplemental Material.

Figure 2 (Fig. 3) summarizes the dependence of the parameters of the unitary transformation between the preferred and excitonic (local) basis on the reorganization energy and the trapping time at the RC. The trapping is assumed to be governed by the localized Liouvillian, see Eq. (13). When the trapping at the RC is so slow that $\tau_{RC}$ is (much) longer than characteristic time scales for excitation dephasing and energy relaxation, phases $\Delta_{px}$ and $\Delta_{pl}$ tend to zero, see Figs. 2(a) and 3(a) for $\tau_{RC} \sim 20 \text{–} 100 \text{ ps}$. These time scales are still much shorter than those relevant for recombination. Therefore, the obtained NESS is expected to be quite similar to the equilibrium state of an undriven and unloaded aggregate. To confirm this expectation, in Figs. 4(a) and 4(b) we plot angles $\theta_{px}$ and $\theta_{pl}$ as functions of the reorganization energy for different values of $\tau_{RC}$. We conclude that, as $\tau_{RC}$ is increased, angles $\theta_{px}$ and $\theta_{pl}$ tend to the values specific of the thermal equilibrium of undriven and unloaded dimer (in which we may formally identify $\tau_{RC}; \tau_{rec} \to +\infty$). For small reorganization energies, angle $\theta_{px}$ tends to zero, see Fig. 4(a), and the preferred basis is close to the excitonic basis. At the same time, the limiting value reached by $\theta_{pl}$ as the reorganization energy is decreased, see Fig. 4(b), corresponds

In brief, we selectively and resonantly ($h\omega_c = \varepsilon_0$) excite site 0 by weak-intensity radiation whose coherence time $\tau_c$ assumes the value representative of the natural Sunlight. The difference $\Delta\varepsilon_{01} = \varepsilon_0 - \varepsilon_1$ between the local energy levels, resonance coupling $J_{01}$, and bath coupling time $\gamma_{01}$, see Eqs. (6) and (9). The time scale of the excitation harvesting, which is governed by Eq. (18) or Eq. (19), is $\tau_{rec}$. The time scale of the excitation loss in recombination events, which is governed by Eq. (20), is $\tau_{RC}$. The reported values of the reorganization energy in the FMO complex range from tens to hundreds of inverse centimeters. Having all these things considered, the values of $\tau_{RC}$ and $\lambda$ will be varied in wide, yet physically relevant ranges, in order to examine how they impact the properties of the NESS.
FIG. 2. (Color online) Dependence of transformation parameter (a) $\Delta_{px}$ and (b) $\theta_{px}$ between the preferred and excitonic basis on the reorganization energy $\lambda$ and the trapping time $\tau_{RC}$ at the RC. Trapping at the RC is governed by the localized-trapping Liouvillian [Eq. (18)]. Both axes feature logarithmic scale, the scale of the color bar in (a) is linear, while that of the color bar in (b) is logarithmic. The maximal value on the color bar in (a) is $\pi/4$.

To the angle of the rotation by which the excitonic basis is transformed into the local basis (the mixing angle $\theta_{xl}$ is given as $\tan(2\theta_{xl}) = 2J_{01}/\Delta_{01}$). As the reorganization energy is increased, the preferred basis continuously changes from the excitonic basis [in which $H_M$ is diagonal, see Eq. (4)] towards the local basis [in which $H_{M-B}$ is diagonal, see Eq. (5)]. Therefore, the magnitude of $\theta_{px}$ increases, see Fig. 4(a), while the magnitude of $\theta_{pl}$ decreases, see Fig. 4(b), with increasing reorganization energy.

On the other hand, when the trapping at the RC is faster, phases $\Delta_{px}$ and $\Delta_{pl}$ increase in magnitude, see Figs. 2(a) and 3(a), while the values of angles $\theta_{px}$ and $\theta_{pl}$ start to deviate from the respective values in the thermal equilibrium, see Figs. 2(b) and 3(b). These deviations are more pronounced as the trapping time is decreased and the reorganization energy is increased, see the lower right corners of Figs. 2(b) and 3(b). At the same time, the magnitude of phase $\Delta_{px}$ is large in the region of fast trapping and relatively small reorganization energy, see the lower left corner of Fig. 2(a), while the increase that $|\Delta_{pl}|$ displays as the trapping time is reduced is virtually the same for all considered values of reorganization energy, see Fig. 3(a). It was suggested that the trapping time practically determines the temporal frame in which the intrinsic dimer’s dynamics is interrogated. It is therefore interesting to examine if the dependence of the transformation parameters between the excitonic (or site) and the preferred basis of the NESS on the trapping time (vertical cuts in Figs. 2 and 3) can be somehow recovered from the dynamics of the unloaded dimer initiated by suddenly turned-on incoherent light. To this end, we propagate the temporal counterparts of Eqs. (10) and (11), in which the trapping and recombination Liou-

FIG. 3. (Color online) Dependence of transformation parameter (a) $\Delta_{pl}$ and (b) $\theta_{pl}$ between the preferred and local basis on the reorganization energy $\lambda$ and the trapping time $\tau_{RC}$ at the RC. Trapping at the RC is governed by the localized-trapping Liouvillian [Eq. (18)]. Both axes feature logarithmic scale, the scale of the color bar in (a) is linear, while that of the color bar in (b) is logarithmic. The maximal value on the color bar in (a) is $\pi/4$. 
FIG. 4. (Color online) Dependence of transformation parameter (a) $\theta_{px}$ (between the preferred and excitonic basis) and (b) $\theta_{pl}$ (between the preferred and site basis) on the reorganization energy $\lambda$ for fixed values of the trapping time at the RC ($\tau_{RC} = 25, 50$ and $100$ ps) and for the undriven and unloaded dimer (formally, $\tau_{RC}, \tau_{rec} \to +\infty$). Trapping at the RC is governed by the localized-trapping Liouvillian [Eq. (18)].

The simple relation between the NESS and RDM dynamics in real time implicitly leans on the fact that the trapping time scale is long enough. Namely, in time traces of a driven and unloaded dimer for $t \gtrsim 1$ ps, one observes that the behavior of both exciton populations [Figs. 5(a1)–(d1)] and interexciton coherences [Figs. 5(a2)–(d2)] displays certain steadiness. In other words, populations, as well as the real part of the interexciton coherence, linearly increase in time, while the imaginary part of the interexciton coherence reaches a constant value, see also the accompanying paper. When the trapping time constant is $\tau_{RC} \gtrsim 1$ ps, so that at $t = \tau_{RC}$ the steadiness has already been established, the dynamical quantities of a driven, but unloaded dimer, may be used to quite accurately reconstruct the NESS. On the other hand, when $\tau_{RC} \lesssim 1$ ps, so that the steadiness has not been established yet, the reconstruction of the NESS from the quantities of a driven and unloaded dimer computed at $\tau_{RC}$ would be less accurate. This is particularly clear for low values of the reorganization energy, see Figs. 5(a3) and 5(a4), when oscillations in the interexciton coherence are damped on a time scale of $\sim 200 – 300$ fs, see Fig. 5(b1). A similar situation can be expected for slow bath, when the bath correlation time $\gamma^{-1}$ is long enough. In such cases, the reconstruction of NESS from the dynamics of the incoherently driven and unloaded dimer is not accurate when $\tau_{RC}$ is comparable to the temporal scale on which dynamical effects originating from the sudden turn-on of light are still present. This time scale is intimately connected to the decay time of interexciton coherence following a delta-like excitation of the dimer, which is in principle accessible in ultrafast spectroscopic experiments. Therefore, the decay time of dynamical coherences observed in spectroscopies may still be relevant in the natural setting, although the dynamical coherences themselves are absent in the NESS. In Sec. SIII of the Supplementary Material, we estimate the time scales characteristic of exciton decoherence by suitable fitting procedures. For the values of model parameters adopted in this work, we find that the characteristic decay times of exciton coherence are shorter than reasonable values of $\tau_{RC}$.

The previous discussion was conducted for interexciton coherences. Similar conclusions can be also reached in the site basis, see Fig. 5. While we have already discussed the limit of long trapping time in Fig. 5(b), the case of relatively short $\tau_{RC} \sim 1 – 10$ ps is analyzed in greater detail in Fig. S2 of the Supplementary Material. The
FIG. 5. (Color online) (a1)–(d1): Time dependence of populations of exciton states $|x_0\rangle$ (solid line) and $|x_1\rangle$ (dashed line) of the incoherently driven and unloaded model dimer for different values of the reorganization energy. (a2)–(d2): Time dependence of the real (solid line) and imaginary (dashed line) parts of the interexciton coherence of the incoherently driven and unloaded model dimer for different values of the reorganization energy. Both exciton populations and interexciton coherences are measured in units of $I_0 d_{eg}^2/\hbar \gamma^2$. The excitation is suddenly turned on at $t = 0$. Dependence of the transformation parameters $\Delta_{px}$ [(a3)–(d3)] and $\theta_{px}$ [(a4)–(d4)] between the excitonic basis and the preferred basis of the NESS on the trapping time constant $\tau_{RC} \in (1,10)$ ps for different values of the reorganization energy. Solid lines are computed using time traces of a driven and unloaded model dimer at $t = \tau_{RC}$, while squares emerge from the computation of the NESS using Eqs. (10) and (11). The scale on the abscissa ($\tau_{RC}$) in (a3)–(d4) is logarithmic. Trapping at the RC is governed by the localized-trapping Liouvillian [Eq. (18)]. The values of the reorganization energy are $20 \text{ cm}^{-1}$ [(a1)–(a4)], $50 \text{ cm}^{-1}$ [(b1)–(b4)], $200 \text{ cm}^{-1}$ [(c1)–(c4)], and $400 \text{ cm}^{-1}$ [(d1)–(d4)].

The choice of instant $t = \tau_{RC}$ at which time-dependent quantities are extracted to obtain the properties of the NESS is somewhat arbitrary because $\tau_{RC}$ is not really the time, but the characteristic time scale of the trapping. Moreover, in the results presented so far, we used the trapping Liouvillian [Eq. (18)] that is diagonal in the local basis. It is, therefore, not obvious if and how the above-discussed relation between the dynamic and stationary pictures under incoherent driving changes when the trapping Liouvillian that is diagonal in the excitonic basis, Eq. (19), is employed. In Figs. (a) and (b), which are analogous to Figs. 2(a) and 2(b), respectively, we examine the dependence of the transformation parameters $\Delta_{px}$ and $\theta_{px}$ on $\lambda$ and $\tau_{RC}$ under the assumption of delocalized trapping. The main features of Figs. (a) and (b) are clearly recognizable in Figs. (a) and (b). This is particularly true at long trapping times. However, at short trapping times, the maximum that $|\Delta_{px}|$ reaches in Fig. 2(a) at $\tau_{RC} \sim 2 - 3$ ps is shifted towards $\tau_{RC} \sim 1 - 2$ ps in Fig. 6(a). A similar discussion applies to Fig. 6(b), where the decrease that $\theta_{px}$ exhibits as $\tau_{RC}$ is increased from 1 ps is shifted to shorter trapping times with respect to Fig. 2(b). We believe that the maximum in $|\Delta_{px}|$, which occurs at $\tau_{RC} \sim 1 - 2$ ps for delocalized trapping, should still be interpreted to originate from the fact that the real part of the interexciton coherence in the driven and unloaded dimer changes its sign on a picosecond time scale. If the real part of the
interexciton coherence is equal to zero at instant $t_0$, it is not guaranteed that the magnitude of $\Delta_{px}$ (computed from the NESS) reaches its maximal value of $\pi/4$ exactly at $\tau_{RC} = t_0$ (this is also observed in Figs. 5(c1)–5(c4)]. Our point here is that the magnitude of $\Delta_{px}$ reaches $\pi/4$ at $\tau_{RC} \sim t_0$ irrespective of the precise form of the trapping Liouvillian.

In the following, we discuss how the variations in the electronic parameters of the model, in particular in the difference $\Delta\varepsilon_{01}$ between local energy levels, affect the properties of the NESS. We fix the reorganization energy to 150 cm$^{-1}$. Figures 7(a) and 7(b) present the dependence of transformation parameters $\Delta_{px}$ and $\theta_{px}$ on $\tau_{RC}$ and $\Delta\varepsilon_{01}$. We varied $\Delta\varepsilon_{01}$ from 30 to 300 cm$^{-1}$ on the basis of the literature values of site-energy differences in the FMO complex.$^{64,74}$ Let us first focus on the long trapping times, when the magnitude of the phase $\Delta_{px}$ is small, see the upper half of Fig. 7(a), and the NESS obtained is quite similar to the excited-state equilibrium. For small values of $\Delta\varepsilon_{01}$, for which $J_{01}/\Delta\varepsilon_{01} \gtrsim 2$, exciton delocalization prevails over the localizing effect of the environment, which is reflected in relatively small values of the rotation angle $\theta_{px}$, see the upper left part of Fig. 7(b). As the local energy levels become more off-resonant, the environment-induced localization becomes more pronounced than exciton delocalization, so that the rotation angle from the excitonic basis to the preferred basis of the NESS increases. However, when $\Delta\varepsilon_{01}$ is large enough, so that $\Delta\varepsilon_{01}/J_{01} \gtrsim 2$, the excitonic basis is already localized enough and, for the chosen value
of $\lambda$, the localizing effect of the environment is effectively suppressed. This leads to a decrease in the rotation angle $\theta_{px}$. As the trapping time is shortened, the deviations from the above-established picture become more pronounced. The magnitude of $\Delta_{px}$ reaches its maximum at $\tau_{RC} = 1 - 10$ ps depending on the particular value of $\Delta_{01}$, see Fig. 7(a), while angle $\theta_{px}$ exhibits a minimum in the very same region of the $\Delta_{01} - \tau_{RC}$ space, see Fig. 7(b).

VI. DISCUSSION AND CONCLUSION

We have provided a detailed and rigorous theoretical description of the light harvesting by a molecular aggregate under conditions that are representative of photosynthetic light harvesting as it occurs in Nature. The picture established in this work takes into account the excitation generation by means of weak incoherent light, their subsequent relaxation and dephasing, as well as excitation trapping by a load (the RC) and recombination. While the generation, relaxation, and dephasing are described in a (numerically) exact manner, which we have reported in the accompanying paper, the excitation trapping and recombination are included on the level of effective Liouvillians.

This piece of research addresses a recurrent question of the possible relevance of quantum coherent effects (understood in a very broad sense) for the natural light harvesting. Our NESS approach provides a physically transparent definition of the light-harvesting efficiency [Eq. (16)] that is basis-invariant, so that we are in position to embark upon the study of possible coherent enhancements of the efficiency. Recent reports have suggested that these coherent enhancements strongly depend on the basis in which the effective trapping and/or recombination Liouvillians are diagonal. Here, motivated by the concepts from the decoherence theory, we put forward the idea that the efficiency ultimately depends only on the diagonal elements (populations) in the preferred basis of the NESS, in which the long-time (steady-state) RDM is diagonal. Because of the basis invariance, possible non-zero coherences in any basis have no impact on the efficiency value, which is essentially set by the properties of the preferred basis. The aforementioned definition of the preferred basis implies that this basis sublines the joint effect of excitation generation, relaxation, dephasing, trapping, and recombination. While finding the preferred basis is highly nontrivial, as demonstrated throughout this paper, this concept sheds new light on the debate on coherent efficiency enhancements.

We have examined the properties of the preferred basis of the NESS of an incoherently driven and loaded dimer. The recombination time scale is, in general, significantly longer than any other time scale in the problem, so that, in the limit of long trapping time, the NESS is very similar to the previously studied excited-state equilibrium of an undriven and unloaded system. We also find that the NESS under driving and load carries information that is encoded in the temporal evolution of the unloaded system driven by suddenly turned-on incoherent light. If the radiation is abruptly turned on at $t = 0$, the properties of the NESS which arises due to the excitation trapping with time constant $\tau_{RC}$ can be quite reliably extracted from the RDM at $t \sim \tau_{RC}$. We conclude that the trapping time scales for which such a relation between the NESS and the dynamics of the driven but unloaded system is sensible are basically determined by the time scales of dephocherence and relaxation, which are accessible in ultrafast spectroscopy experiments. Since realistic trapping times are in general much longer than decoherence and relaxation time scales, the relation we found between the steady-state and time-dependent pictures is quite general.

We again note that our theoretical and computation approach to obtain the NESS under incoherent driving is general and not limited to the model dimer studied here. We opted for the dimer because the relationships between basis vectors of the preferred basis and the excitonic or local basis can be parameterized by only two real parameters, which have certain physical significance and whose dependence on model parameters can be studied in a systematic manner. In the case of a more complex excitonic aggregate, one should resort to more involved parameterizations of unitary matrices.

SUPPLEMENTARY MATERIAL

See supplementary material for: (a) the derivation of equations for the transformation parameters $\theta$ and $\Delta$; (b) detailed numerical procedure to compute the nonequilibrium steady state; (c) analysis of the dynamics initiated by a delta-like photoexcitation; (d) the comparison of transformation parameters $\theta_d$ and $\Delta_d$ obtained from stationary and time-dependent pictures in the case of fast trapping.

ACKNOWLEDGMENTS

The initial stages of this work were supported by Charles University Research Center program No. UNCE/SCI/010. The final stages of this work were supported by the Institute of Physics Belgrade, through the grant by the Ministry of Education, Science, and Technological Development of the Republic of Serbia. Computational resources were supplied by the project "e-Infrastruktura CZ" (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures. Numerical computations were also performed on the PARADOX supercomputing facility at the Scientific Computing Laboratory of the Institute of Physics Belgrade.
AUTHOR’S CONTRIBUTIONS

T.M. gave the initial impetus for this work, which started during V.J.’s stay in Prague. V.J. developed the methodology, conducted all numerical computations, analyzed their results, and prepared the initial version of the manuscript. Both authors contributed to the submitted version of the manuscript.

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SI. DERIVATION OF EXPRESSIONS FOR TRANSFORMATION PARAMETERS $\theta$ AND $\Delta$

Here, we discuss in greater detail the expressions for the transformation parameters $\theta_{px}$ and $\Delta_{px}$ between the exciton basis and the preferred basis of the NESS. The discussion in the case of localized basis is analogous.

The normalized RDM in the $ee$ sector, $\hat{\rho}_{ee}^{N}$, is expressed in the preferred basis of the NESS and the exciton basis as follows

$$\hat{\rho}_{ee}^{N} = \sum_{i} \tilde{p}_{i} |p_{i}\rangle \langle p_{i}| = \sum_{jk} \left( \sum_{i} |x_{j}| \langle x_{j}| \tilde{p}_{i} \langle p_{i}| x_{k}\rangle \right) |x_{j}\rangle \langle x_{k}|.$$  \hfill (S1)

On the other hand, the expression for $\hat{\rho}_{ee}^{N}$ in terms of Pauli matrices

$$\sigma_{1} = |x_{0}\rangle \langle x_{1}| + |x_{1}\rangle \langle x_{0}|,$$

$$\sigma_{2} = -i (|x_{0}\rangle \langle x_{1}| - |x_{1}\rangle \langle x_{0}|),$$

$$\sigma_{3} = |x_{0}\rangle \langle x_{0}| - |x_{1}\rangle \langle x_{1}|$$  \hfill (S2)

reads as

$$\hat{\rho}_{ee}^{N} = \frac{1}{2} \left( (1 + a_{3}^{x}) |x_{0}\rangle \langle x_{0}| + (a_{3}^{x} - i a_{5}^{x}) |x_{0}\rangle \langle x_{1}| + (a_{3}^{x} + i a_{5}^{x}) |x_{1}\rangle \langle x_{0}| + (1 - a_{3}^{x}) |x_{1}\rangle \langle x_{1}| \right).$$  \hfill (S3)

Using Eqs. (S1) and (S3) together with Eq. (23) of the main text we obtain

$$a_{3}^{x} = (2 \tilde{p}_{0} - 1) \cos(2\theta_{px}) = (1 - 2 \tilde{p}_{1}) \cos(2\theta_{px})$$  \hfill (S4)

$$a_{3}^{x} - i a_{5}^{x} = (2 \tilde{p}_{0} - 1) e^{i2\Delta_{px}} \sin(2\theta_{px}).$$  \hfill (S5)

The relationships between the Bloch angles $\theta_{p}^{x}$ and $\phi_{p}^{x}$ and transformation parameters $\theta_{px}$ and $\Delta_{px}$ that presented in the main body of the manuscript now become apparent.

Let us now discuss the range in which $\theta_{px}$ and $\Delta_{px}$ may always be chosen. The Pauli matrices may be chosen as in Eq. (S2) and we this choice will be termed choice 1. There is, however, choice 2, in which $|x_{0}\rangle$ and $|x_{1}\rangle$ are permuted

$$\sigma_{1} = |x_{1}\rangle \langle x_{0}| + |x_{0}\rangle \langle x_{1}|,$$

$$\sigma_{2} = -i (|x_{1}\rangle \langle x_{1}| - |x_{0}\rangle \langle x_{0}|),$$

$$\sigma_{3} = |x_{1}\rangle \langle x_{1}| - |x_{0}\rangle \langle x_{0}|.$$  \hfill (S6)

Then, $a_{3}^{x(1)} = -a_{3}^{x(2)}$, $a_{5}^{x(1)} = -a_{5}^{x(2)}$, and $a_{1}^{x(1)} = a_{1}^{x(2)}$, so that

$$\cos(2\theta_{px}^{(1)}) + \cos(2\theta_{px}^{(2)}) = 2 \cos(\theta_{px}^{(1)}) \cos(\theta_{px}^{(2)}) \cos(\phi_{px}^{(1)} - \phi_{px}^{(2)}) = 0,$$  \hfill (S7)

$$\tan(2\Delta_{px}^{(1)}) + \tan(2\Delta_{px}^{(2)}) = \left( 1 - \tan(2\Delta_{px}^{(1)}) \tan(2\Delta_{px}^{(2)}) \right) \tan(2\Delta_{px}^{(1)} + 2\Delta_{px}^{(2)}) = 0.$$  \hfill (S8)

It then follows that ($k$ is an integer)

$$\theta_{px}^{(2)} = \frac{\pi}{2} \pm \theta_{px}^{(1)} + k\pi,$$

$$\Delta_{px}^{(2)} = -\Delta_{px}^{(1)} + k\frac{\pi}{2}.$$  \hfill (S9)

From Eq. (S4), we know that $\theta_{px}^{(1)} \in (0, \pi/2)$, so that the rotation angle $\theta_{px}^{(2)}$ can always be chosen so that $\theta_{px}^{(2)} \in (0, \pi/4)$. Equation (S9) suggests that such a choice for $\theta_{px}$ may result in the phase $\Delta_{px}$ acquiring an additional minus sign, which, however, does not affect the range $(-\pi/4, \pi/4)$ of possible values for $\Delta_{px}$. It is for this reason that in Figs. 2–7 of the main text we plot the magnitude $|\Delta_{px}|.$

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SII. COMPUTATION OF THE NONEQUILIBRIUM STEADY STATE

As mentioned in the main body of the manuscript, the computational algorithm to obtain the NESS leans on the method proposed in Ref. [3] to compute the excited-state equilibrium of a molecular aggregate. The method exploits the fact that the computation of the HEOM steady state can be seen as solving a system of linear algebraic equations, which can be done in an iterative way using, e.g., the Jacobi iteration method. However, the Jacobi iteration method relies on the diagonal dominance of the system, an assumption that is, in general, not satisfied in our problem, especially in the regimes of intermediate and strong system–bath coupling. Equations (10) and (11) of the main text are the basis for the following iterative procedure to compute the ADMs $\sigma_{eg,n}^{ss,new}$ and $\sigma_{ee,n}^{ss,new}$ in the current iteration using the ADMs $\sigma_{eg,n}^{ss,old}$ and $\sigma_{ee,n}^{ss,old}$ from the previous iteration.

\[
\left(\frac{i}{\hbar}\omega_{eg} + \gamma_{n} + (\tau_{c} \gamma)^{-1} + \epsilon\right) \langle x \mid \sigma_{eg,n}^{ss,new} \mid g \rangle = \epsilon \langle x \mid \sigma_{eg,n}^{ss,old} \mid g \rangle - \frac{\Delta}{\hbar^2 \gamma} \sum_{j} \langle x \mid V_{j} \sigma_{eg,n}^{ss,old} \mid g \rangle + \delta_{n,0} \frac{i}{\hbar \gamma} \langle x \mid J_{0} \mid g \rangle + \frac{1}{\hbar \gamma} \langle x \mid \mu_{eg} \mid g \rangle^{*} + \frac{1}{\hbar \gamma} \langle x \mid \mu_{eg} \mid g \rangle + \gamma^{-1} \langle x \mid C_{c}(\sigma_{eg,n}^{ss,old}) \mid \bar{x} \rangle + \gamma^{-1} \langle x \mid C_{c}(\sigma_{eg,n}^{ss,old}) \mid \bar{x} \rangle
\]

\[
\left(\frac{i}{\hbar}\omega_{ee} + \gamma_{n} + \epsilon\right) \langle x \mid \sigma_{ee,n}^{ss,new} \mid \bar{x} \rangle = \epsilon \langle x \mid \sigma_{ee,n}^{ss,old} \mid \bar{x} \rangle - \frac{\Delta}{\hbar^2 \gamma} \sum_{j} \langle x \mid V_{j} \times V_{j} \times \sigma_{ee,n}^{ss,old} \mid \bar{x} \rangle + \frac{1}{\hbar \gamma} \langle x \mid \mu_{ee} \mid g \rangle^{*} + \frac{1}{\hbar \gamma} \langle x \mid \mu_{ee} \mid g \rangle + \gamma^{-1} \langle x \mid C_{c}(\sigma_{ee,n}^{ss,old}) \mid \bar{x} \rangle + \gamma^{-1} \langle x \mid C_{c}(\sigma_{ee,n}^{ss,old}) \mid \bar{x} \rangle
\]

In Eqs. (S10) and (S11), $\langle x \rangle$ and $\langle \bar{x} \rangle$ are exciton states, $\hbar \omega_{x}$ and $\hbar \omega_{e}$ are their respective vertical excitation energies, while $\epsilon$ is an adjustable parameter whose value should be tuned so that the steady-state HEOM becomes a diagonally dominant system of linear algebraic equations. The value of $\epsilon$ should be chosen so as to reach a compromise between algorithm stability and numerical accuracy (large $\epsilon$) on the one hand and numerical effort (small $\epsilon$) on the other hand.

Equations (S10) and (S11) are solved in the exciton basis because their free-evolution parts are diagonal in that basis, see the $c$-numbers that multiply the ADM elements in the current iteration on the left-hand sides of these equations. When the trapping and/or recombination Liouvilleans are known to be diagonal in the exciton basis, they may be treated in the same manner as the free-evolution terms, which would lead to a more complicated form of the $c$-numbers appearing on the left-hand sides of Eqs. (S10) and (S11).

The iterative procedure is terminated once the continuity equation [Eq. (10) of the main text] is satisfied with the desired numerical accuracy $\delta$. In more detail, we use the following termination criterion.

\[
\frac{|J_{gen} - J_{RC} - J_{rec}|}{\min \{J_{gen}, J_{RC}, J_{rec}\}} < \delta.
\]

Our numerical computations suggest that the quantity on the left-hand side of Eq. (S12) monotonously decreases as the algorithm proceeds, so that the termination criterion is sensible. We also monitor changes the ADM elements...
undergo upon one iteration of the algorithm by following the changes in the following quantities

\[ E_{ee} = \max_{n, \bar{x}, \bar{x}'} \left\{ |f(n)|^{-1} \left| \langle \bar{x} | \sigma_{ee, n}^{ss, \text{new}} | \bar{x} \rangle - \langle \bar{x} | \sigma_{ee, n}^{ss, \text{old}} | \bar{x} \rangle \right| \right\}, \quad (S13) \]

\[ E_{eg} = \max_{n, \bar{x}, \bar{x}'} \left\{ |f(n)|^{-1} \left| \langle \bar{x} | \sigma_{eg, n}^{ss, \text{new}} | \bar{x} \rangle - \langle \bar{x} | \sigma_{eg, n}^{ss, \text{old}} | \bar{x} \rangle \right| \right\}, \quad (S14) \]

where the rescaling factor \( f(n) \) reads as

\[ f(n) = \prod_{j} \prod_{m=0}^{K-1} \left( \left( \frac{\epsilon_{m}}{(\hbar \gamma)_{j}} \right)^{n_{j, m}} \right)^{-1/2}. \quad (S15) \]

We observe that the quantities \( E_{ee} \) and \( E_{eg} \) monotonically decrease during the course of the algorithm, another sign that our procedure for determining the NESS should lead to correct results.

Another important ingredient of the algorithm is the initial guess for the iterative procedure embodied in Eqs. (S10) and (S11). In Ref. 1, which dealt with the excited-state equilibrium, the initial condition was the purely electronic density matrix in the absence of the environment, i.e., \( e^{-\beta \mathcal{H}_M} / \text{Tr}_M \{ e^{-\beta \mathcal{H}_M} \} \). Here, however, we have incoherent driving, trapping, and recombination, so that a natural initial guess for the NESS can be obtained by solving the corresponding Redfield equation. In our companion paper, we presented the derivation of the Redfield equation under driving.\(^3\) The appropriate modifications to take into account excitation trapping and recombination are described in the main body of the manuscript. The corresponding steady-state Redfield equations in the \( eg \) and \( ee \) sectors read as

\[ 0 = -i \left( \frac{\omega_x - \omega_c}{\gamma} - i(\tau_c) \right) \langle \bar{x} | \rho_{ee}^{ss} | g \rangle + \frac{1}{\hbar \gamma} \langle \bar{x} | \mu_{eg} | g \rangle - \gamma^{-1} \sum_{\bar{x}'} \left( \sum_{\bar{x}} \mathrm{Re} \Gamma_{\bar{x} \bar{x}' \bar{x}'} \right) \langle \bar{x}' | \rho_{eg}^{ss} | g \rangle, \quad (S16) \]

\[ 0 = -i \left( \frac{\omega_x - \omega_c}{\gamma} \right) \langle \bar{x} | \rho_{ee}^{ss} | \bar{x} \rangle + \langle \bar{x} | \mu_{eg} | g \rangle - \gamma^{-1} \sum_{\bar{x}' \bar{x}'} \left( \sum_{\bar{x}} \mathrm{Re} \Gamma_{\bar{x} \bar{x}' \bar{x}'} + \delta_{\bar{x}' \bar{x}} \sum_{\bar{x}} \mathrm{Re} \Gamma_{\bar{x} \bar{x}' \bar{x}'} - \delta_{\bar{x}' \bar{x}} \sum_{\bar{x}} \mathrm{Re} \Gamma_{\bar{x} \bar{x}' \bar{x}'} \right) \langle \bar{x}' | \rho_{eg}^{ss} | \bar{x}' \rangle + \gamma^{-1} \langle \bar{x} | \mathcal{L}_{\text{rec}}[\rho_{ee}^{ss}] | \bar{x} \rangle \quad (S17) \]

where the tetratic quantity \( \Gamma_{\bar{x} \bar{x}' \bar{x}''} \) is

\[ \Gamma_{\bar{x} \bar{x}' \bar{x}'} = \sum_{\bar{x}} \langle \bar{x} | j \rangle \langle j | \bar{x}' \rangle \langle \bar{x}' | j \rangle \langle j | \bar{x}' \rangle \int_{-\infty}^{+\infty} ds \frac{C(s)}{\hbar^2} \exp \left( i(\omega_x - \omega_c)s \right). \quad (S18) \]

In Eqs. (S16) and (S17), we follow a common practice and neglect imaginary parts of \( \Gamma_{\bar{x} \bar{x}' \bar{x}'} \). For the Drude–Lorentz spectral density, and under the assumption of purely real exciton wave functions \( \langle j | x \rangle \), the corresponding real parts can be computed analytically to yield

\[ \mathrm{Re} \Gamma_{\bar{x} \bar{x}' \bar{x}'} = \left[ \sum_{\bar{x}} \langle \bar{x} | j \rangle \langle j | \bar{x}' \rangle \langle \bar{x}' | j \rangle \langle j | \bar{x}' \rangle \right] C(\omega_x - \omega_c), \quad (S19) \]

where

\[ C(\omega) = \mathrm{Re} \int_{0}^{+\infty} ds \frac{C(s) \exp \omega s}{\hbar^2} = \begin{cases} \frac{\lambda}{\gamma} & \omega > 0; \\ \frac{2}{\gamma^2} & \omega < 0; \\ 2 \times \frac{\lambda}{\gamma} & \omega = 0. \end{cases} \quad (S20) \]

Upon solving Eqs. (S16) and (S17), we explicitly check that the continuity equation \( J_{\text{gen}} - J_{\text{rec}} - J_{\text{RC}} = 0 \) is satisfied.

The convergence of the HEOM method should always be checked against the maximal depth of the hierarchy and the number of terms in the optimized exponential series for the bath correlation function. Let us first concentrate on the convergence with respect to the depth of the hierarchy. We gradually increase the depth of the hierarchy in the following manner:
1. we start with Eqs. (S10) and (S11) up to depth $D = 2$; the initial guess for the RDM is obtained by solving Eqs. (S16) and (S17), while the ADMs on depths 1 and 2 are set to zero; the numerical accuracy with which the continuity equation is satisfied is set to $\delta_2$, see Eq. (S12);

2. we use the solution up to depth $D \geq 2$ as the initial guess for the computations up to depth $D + 2$ (the ADMs at depths $D + 1$ and $D + 2$ are set to zero); the numerical accuracy with which the continuity equation is satisfied in the computation up to depth $D + 2$ is $\delta_{D+2} = c \cdot \delta_D$, where $c < 1$ (if the numerical accuracy is not downscaled, the algorithm at depth $D + 2$ terminates immediately).

In this manner, we are able to check how the quantities of our interest, in particular transformation parameters between exciton/localized basis and the preferred basis of the NESS, depend on the maximal depth of the hierarchy. For the values of model parameters summarized in Table I of the main text, the deepest hierarchy is constructed for the largest reorganization energy ($\lambda = 400 \text{ cm}^{-1}$), and its depth is 14.

We now briefly discuss the convergence of the HEOM with respect to $K$, and concentrate on the values of model parameters listed in Table I of the main text. These values satisfy the low-temperature approximation $\beta \hbar \gamma \ll 1$ reasonably well. When the interaction with the environment is weak, the steady-state Redfield equations [Eqs. (S16) and (S17)] should present a good description of the situation of our interest. From Eqs. (S18)–(S20), we see that, in this case, the relaxation tensor depends on the full spectral density, so that we should have $K > 1$. We have checked that $K = 3$ is a reasonable choice for the weak coupling to the environment. On the other hand, for stronger excitation–environment coupling, we have numerically verified that it is enough to take $K = 1$. 

SIII. ANALYSIS OF THE DYNAMICS INITIATED BY A δ-LIKE PHOTOEXCITATION

Here, we analyze in greater detail the dynamics of the model dimer initiated by an impulsive photoexcitation and extract the time scales of such dynamics. In particular, we examine time dependence of the real and imaginary part of the interexciton coherence on a picosecond time scale following a sudden δ-like excitation at $t = 0$. The real part of the interexciton coherence is fitted using

$$\text{Re} \{\rho_{01}(t)\} = a_0 + a_1 e^{-t/a_2} \cos(a_3 t) + a_4 e^{-t/a_5} + a_6 e^{-t/a_7},$$

(S21)

while the fitting function for the imaginary part reads as

$$\text{Im} \{\rho_{01}(t)\} = b_1 e^{-t/b_2} \sin(b_3 t) + b_4 e^{-t/b_5} + b_6 e^{-t/b_7}.$$

(S22)

In Fig. SI, we present the results of computations and fit, while the best values of fitting parameters are summarized in Tables SI–SIV.
FIG. SI. Time dependence of the real (left column) and imaginary (right column) part of the interexciton coherence following a sudden δ-like excitation of the model dimer. Solid lines are obtained by propagating HEOM, while dashed lines are best fits to numerical data using the fitting functions given in Eqs. S21 and S22. The best fitting parameters are summarized in Tables SI–SIV.
TABLE SI. Fitting Parameters for $\lambda = 20$ cm$^{-1}$.

| Parameter (Unit) | Value          |
|------------------|----------------|
| $a_0$ (-)        | $2.96 \times 10^{-3}$ |
| $a_1$ (-)        | -0.3933        |
| $a_2$ (fs)       | 193.9          |
| $h\alpha_3$ (cm$^{-1}$) | 228.5         |
| $a_4$ (-)        | -0.091         |
| $a_5$ (fs)       | 84             |
| $a_6$ (-)        | 0.010          |
| $a_7$ (fs)       | 300            |
| $b_1$ (-)        | 0.4460         |
| $b_2$ (fs)       | 192.8          |
| $h\beta_3$ (cm$^{-1}$) | 229.1         |
| $b_4$ (-)        | -0.0277        |
| $b_5$ (fs)       | 103            |
| $b_6$ (-)        | 0.0209         |
| $b_7$ (fs)       | 282            |

TABLE SII. Fitting Parameters for $\lambda = 50$ cm$^{-1}$.

| Parameter (Unit) | Value          |
|------------------|----------------|
| $a_0$ (-)        | $7.24 \times 10^{-3}$ |
| $a_1$ (-)        | -0.3146        |
| $a_2$ (fs)       | 105.2          |
| $h\alpha_3$ (cm$^{-1}$) | 235.7         |
| $a_4$ (-)        | -0.03135       |
| $a_5$ (fs)       | 277            |
| $a_6$ (-)        | -0.14762       |
| $a_7$ (fs)       | 60.70          |
| $b_1$ (-)        | 0.43085        |
| $b_2$ (fs)       | 99.20          |
| $h\beta_3$ (cm$^{-1}$) | 240.6         |
| $b_4$ (-)        | -0.06465       |
| $b_5$ (fs)       | 165.2          |
| $b_6$ (-)        | 0.0526         |
| $b_7$ (fs)       | 148.0          |
TABLE SIII. Fitting Parameters for $\lambda = 200 \text{ cm}^{-1}$.

| Parameter (Unit) | Value    |
|------------------|----------|
| $a_0$ (-)        | 0.02787  |
| $a_1$ (-)        | −0.163   |
| $a_2$ (fs)       | 51.4     |
| $h a_3$ (cm$^{-1}$) | 230     |
| $a_4$ (-)        | −0.141   |
| $a_5$ (fs)       | 43.9     |
| $a_6$ (-)        | −0.2038  |
| $a_7$ (fs)       | 270.7    |
| $b_1$ (-)        | 0.427    |
| $b_2$ (fs)       | 36.9     |
| $h b_3$ (cm$^{-1}$) | 250     |
| $b_4$ (-)        | −0.0754  |
| $b_5$ (fs)       | 15.92    |
| $b_6$ (-)        | 0.0662   |
| $b_7$ (fs)       | 156.7    |

TABLE SIV. Fitting Parameters for $\lambda = 400 \text{ cm}^{-1}$.

| Parameter (Unit) | Value    |
|------------------|----------|
| $a_0$ (-)        | 0.050754 |
| $a_1$ (-)        | −0.082   |
| $a_2$ (fs)       | 42.80    |
| $h a_3$ (cm$^{-1}$) | 222     |
| $a_4$ (-)        | −0.163   |
| $a_5$ (fs)       | 44.7     |
| $a_6$ (-)        | −0.2746  |
| $a_7$ (fs)       | 446.5    |
| $b_1$ (-)        | 0.8      |
| $b_2$ (fs)       | 19.5     |
| $h b_3$ (cm$^{-1}$) | 170     |
| $b_4$ (-)        | −0.0496  |
| $b_5$ (fs)       | 16       |
| $b_6$ (-)        | 0.0349   |
| $b_7$ (fs)       | 277      |
SIV. TRANSFORMATION PARAMETERS $\theta_{pl}$ AND $\Delta_{pl}$ UNDER FAST TRAPPING

FIG. SII. (a1)–(d1): Time dependence of populations of localized states $|l_0\rangle$ (solid line) and $|l_1\rangle$ (dashed line) of the incoherently driven and unloaded model dimer for different values of the reorganization energy. (a2)–(d2): Time dependence of the real (solid line) and imaginary (dashed line) parts of the intersite coherence of the incoherently driven and unloaded model dimer for different values of the reorganization energy. Both site populations and intersite coherences are measured in units of $I_0 e_{eg}^2/(\hbar \gamma)^2$. The excitation is suddenly turned on at $t = 0$. Dependence of the transformation parameters $\Delta_{px}$ [(a3)–(d3)] and $\theta_{px}$ [(a4)–(d4)] between the localized basis and the preferred basis of the NESS on the trapping time constant $\tau_{RC} \in (1, 10)$ ps for different values of the reorganization energy. Solid lines are computed using time traces of a driven and unloaded model dimer at $t = \tau_{RC}$, while squares emerge from the computation of the NESS using Eqs. (10) and (11) of the main text. The scale on the abscissa ($\tau_{RC}$) in (a3)–(d4) is logarithmic. Trapping at the RC is governed by the localized-trapping Liouvillian [Eq. (18) of the main text]. The values of the reorganization energy are 20 cm$^{-1}$ [(a1)–(a4)], 50 cm$^{-1}$ [(b1)–(b4)], 200 cm$^{-1}$ [(c1)–(c4)], and 400 cm$^{-1}$ [(d1)–(d4)].

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