Exact description of excitonic dynamics in molecular aggregates weakly driven by light

Veljko Janković1,2 and Tomáš Mančal1

1Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
2Scientific Computing Laboratory, Center for the Study of Complex Systems, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Republic of Serbia

We present a rigorous theoretical description of excitonic dynamics in molecular light-harvesting aggregates photoexcited by weak-intensity radiation of arbitrary properties. While the interaction with light is included up to the second order, the treatment of the excitation–environment coupling is exact and results in an exact expression for the reduced excitonic density matrix that is manifestly related to the spectroscopic picture of the photoexcitation process. This expression takes fully into account the environmental reorganization processes triggered by the two interactions with light. This is particularly important for slow environments and/or strong excitation–environment coupling. Within the exponential decomposition scheme, we demonstrate how our result can be recast as the hierarchy of equations of motion (HEOM) that explicitly and consistently includes the photoexcitation step. We analytically describe the environmental reorganization dynamics triggered by a delta-like excitation of a single chromophore, and demonstrate how our HEOM, in appropriate limits, reduces to the Redfield equations comprising a pulsed photoexcitation and the nonequilibrium Förster theory. We also discuss the relation of our formalism to the combined Born–Markov–HEOM approaches in the case of excitation by thermal light.

I. INTRODUCTION

Recent years have seen vigorous interest in unveiling the basic physical mechanisms governing the electronic solar energy conversion in photosynthetic systems [1–4]. The developments in this field are expected to provide new ways of improving the light-to-charge conversion in artificial systems, e.g., organic photovoltaics (OPVs) [5]. A thorough understanding of the solar energy conversion in molecular light-harvesting systems calls for a detailed description of light absorption, excitation energy transfer (EET), charge separation, and charge transport [6, 7]. Our current understanding of these steps has been shaped by ultrafast spectroscopy experiments, which can provide insights into dynamics of electronic excitations on time scales as short as a couple of femtoseconds [8–11]. Such experiments, therefore, can also temporally resolve nuclear motions provoked by photoexcitation, i.e., nuclear reorganization processes, which take place on ∼10–100 fs time scales. Moreover, photosynthetic EET falls into the so-called intermediate regime [2, 3, 12], in which the energy scales representative of electronic couplings, excitation–environment couplings, and static disorder in local transition energies are comparable to one another. Therefore, a proper interpretation of ultrafast experimental signatures necessitates development of explicitly time-dependent theoretical approaches that can accurately capture the non-Markovian dynamical interplay between temporal evolution of electronic excitations and their environment [3, 12]. Examples of such methods include hierarchical equations of motion (HEOM) [13], and some wavefunction-based methods [14].

Apart from the nonperturbative treatment of the interaction with the environment, a comprehensive theoretical analysis of the dynamics of electronic excitations created during ultrafast spectroscopy experiments should explicitly consider the exciting radiation field. However, the explicit inclusion of the photoexcitation process has received only a limited attention so far. The photoexcitation is commonly assumed to be infinitely short, i.e., delta-like, so that it instantaneously produces excited-state populations, whose further evolution on ultrashort time scales is followed [15, 16]. On the other hand, theoretical methods of nonlinear spectroscopy [17], which explicitly keep track of the interaction with exciting pulses, have been employed in conjunction with, e.g., HEOM, to examine certain features of spectroscopic signals [18]. However, there has not been much discussion on how to explicitly include the photoexcitation and respect the nonperturbative treatment of the excitation–environment coupling [19]. The importance of the photoexcitation step is typically discussed within the debate on the relevance of the results of ultrafast experiments for the photosynthetic operation in vivo [20–24]. It is argued that, due to different properties of natural Sunlight compared to laser pulses employed in experiments, photoexcitation of photosynthetic complexes under natural conditions triggers different dynamics from the one observed in ultrafast experiments. Nevertheless, under the common assumption that the electronic system is initially unexcited, any nontrivial dynamics under both excitation conditions is ultimately induced by the interaction with the radiation. In a nonlinear spectroscopy experiment, the signal depends on the appropriate power of the exciting field, i.e., the perturbation expansion in the interac-
tion with radiation is appropriate \cite{17,22}. Similarly, the weakness of the excitation of photosynthetic complexes under natural conditions makes the second-order treatment of the interaction with light plausible \cite{20,22,21}.

Indeed, it has been shown \cite{20} that the excited-state dynamics of a molecular system weakly driven by light of arbitrary properties is completely determined by the first-order radiation correlation function and the reduced evolution superoperator. It can be said that the information required for constructing the dynamics under arbitrary (weak) driving can only be obtained by ultrafast spectroscopy \cite{21}, which provides access to the reduced evolution superoperator. However, the analysis conducted in Ref. \cite{20} is quite general and does not provide any details on the form and properties of this superoperator. Certainly, it should contain information about the nonequilibrium evolution of the environment taking place between consecutive interactions with light \cite{22}. Along these lines, attempts were made to examine the importance of these dynamical environmental effects for the second-order light-induced dynamics by augmenting the usual quantum master equation by terms that depend on the delay between the two interactions \cite{23}. The analysis of the second-order photoinduced dynamics in Ref. \cite{28} suggested that the nonequilibrium bath evolution between the two interactions with light is reflected in the so-called photoinduced correlation term. Let us note that the analyses conducted in Refs. \cite{26,28} are essentially perturbative in the excitation–environment coupling.

On the other hand, in the field of ultrafast semiconductor optics, \cite{24,31}, the photoexcitation step and the nonequilibrium dynamics of thus induced electronic excitations are typically studied within the density matrix (DM) theory complemented with the so-called dynamics controlled truncation (DCT) scheme \cite{23,24}. The DCT scheme classifies DMs according to the lowest power which they scale in the exciting field and, therefore, provides a recipe to analyze the dynamics up to any given order in the exciting field in terms of a finite number of electronic DMs. A DCT-based approach has been recently applied by one of us to study exciton generation and subsequent charge separation in photoexcited OPVs. \cite{23,34}. However, the truncation of the environment-assisted branch of the hierarchy within the DCT scheme still has to be performed separately \cite{31}, and it is commonly done in a low order in the excitation–environment coupling \cite{23,25,26}.

While the explicit inclusion of light–matter coupling is typically accompanied by a perturbative treatment of excitation–environment coupling, there are also studies concentrating on a (numerically) exact treatment of the latter, at the expense of a less transparent inclusion of the former \cite{36,37}. When the semiclassical description of light–matter interaction is appropriate, the time-dependent electric field can be straightforwardly incorporated in the HEOM formalism \cite{35,39}, whose relation to the spectroscopic picture of sequential interactions with light is not manifest. When the quantum description of light–matter interaction is in place \cite{36,37}, the interaction with the radiation is treated from the standpoint of quantum optics, using the so-called hybrid master-equation–HEOM approach \cite{40}. In essence, the interaction with radiation appears in form of Markovian corrections to HEOM equations. In the end, there are also studies that propose a (numerically) exact treatment of both the couplings to environment and radiation \cite{41}, which, however, comes with a complex formalism and huge computational costs.

In this work, we build on results of Ref. \cite{21}. Our approach is based on the two cornerstones of the theory of photosynthetic excitons \cite{12}. Section \textbf{II} introduces the Frenkel exciton model of a molecular light-harvesting aggregate, while the theory of nonlinear spectroscopy is employed in Sec. \textbf{III} to shed new light on the existing approaches \cite{38,39} to include semiclassical light–matter coupling into HEOM formalism. Section \textbf{IV} presents the central result of our analysis. There, we perform a second-order treatment of light–matter coupling and a nonperturbative treatment of excitation–environment coupling to obtain an expression for weak light-induced excitonic dynamics that is manifestly related to the spectroscopic picture, and fully includes the dynamical interplay between nonequilibrium electronic dynamics and environmental reorganization processes. The exact result that we obtain does not allow for easy analytical manipulations, and we demonstrate how it can be recast as HEOM, both in the case of semiclassical (Sec. \textbf{V}) and quantum (Sec. \textbf{VI}) treatment of the interaction with light. In addition, we analytically solve for the environmental reorganization dynamics triggered by a delta-like excitation of a single molecule (Sec. \textbf{V A}), and relate our results to existing approaches, such as the Redfield theory with photoexcitation (Sec. \textbf{V B}), the nonequilibrium Förster theory (Sec. \textbf{VC}), and hybrid Born–Markov–HEOM approaches (Sec. \textbf{VI}). These discussions further emphasize the advantages of our method, which are once again summarized in the concluding Sec. \textbf{VII}.

II. MODEL HAMILTONIAN

The system of interest consists of a molecular aggregate $M$ that is in contact with the thermal bath $B$ representing its environment and with the radiation $R$. The total Hamiltonian reads as

$$H = H_M + H_B + H_R + H_{M-B} + H_{M-R}.$$  \hspace{1cm} (1)

Here, $H_M$ describes electronic excitations of the aggregate, $H_B$ and $H_R$ are the bath and radiation Hamiltonians, respectively, $H_{M-B}$ describes the interaction of electronic excitations of $M$ with the bath $B$, while $H_{M-R}$ accounts for the driving of $M$ by light.

The aggregate consists of $N$ monomers (chromophores, molecules) and we assume that, in addition to the monomer’s ground state, it is enough to consider only one excited state on each monomer. Electronic excitations of
such an aggregate are studied within the Frenkel exciton model \cite{42,43,45} with operators \( B_j^\dagger \) and \( B_j \) describing generation and destruction of excitation on chromophore \( j \), respectively. The Hamiltonian of electronic excitations is formulated in the Heitler–London approximation \cite{42,46}, which is standard in the theory of photosynthetic excitons \cite{42,43,45}, and it is given by

\[
H_M = \sum_j \varepsilon_j B_j^\dagger B_j + \sum_{jk} J_{jk} B_j^\dagger B_k. \tag{2}
\]

In Eq. (2), \( \varepsilon_j \) are the so-called site energies, while \( J_{jk} \) are resonance couplings (we take \( J_{kk} = 0 \)). Operators \( B_j, B_j^\dagger \) are the so-called Paulions and obey the following commutation rules \cite{29,43,45}

\[
[B_j, B_k] = \left[ B_j^\dagger, B_k^\dagger \right] = B_j^2 = \left( B_j^\dagger \right)^2 = 0, \tag{3a}
\]

\[
\left[ B_j, B_k^\dagger \right] = \delta_{jk} \left( 1 - 2B_j^2 B_j^\dagger \right). \tag{3b}
\]

The Hamiltonian \( H_M \) takes into account states with various numbers of excitations present in the aggregate. Therefore, the Hilbert space of aggregate excitations can be decomposed as a direct sum

\[
\mathcal{H}_M = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \ldots \tag{4}
\]

of subspaces accommodating 0, 1, 2, . . . excitations. The subspace \( \mathcal{H}_0 \) is spanned by the vacuum state \( |0\rangle \) (no excitations). The vacuum state corresponds to the collective electronic ground state of the aggregate, commonly denoted as \( |g\rangle \), whose energy sets the zero of the energy scale. The subspace of singly excited states is \( \mathcal{H}_1 = \text{span} \{|j\rangle = B_j^\dagger |0\rangle \} \). The reduction of \( H_M \) to this subspace produces the standard Frenkel exciton Hamiltonian for the singly excited states \cite{43}

\[
(H_M)_{\mathcal{H}_1} = \sum_j \varepsilon_j |j\rangle \langle j| + \sum_{jk} J_{jk} |j\rangle \langle k|. \tag{5}
\]

In a similar manner, the reduction of \( H_M \) to the subspace of doubly excited states \( \mathcal{H}_2 = \text{span} \{ |jk\rangle \equiv B_j^\dagger B_k^\dagger |0\rangle \} \) produces the Frenkel exciton Hamiltonian of the doubly excited aggregate.

The environment is assumed to be composed of sets of harmonic oscillators associated to each site

\[
H_B = \sum_{j, \xi} \hbar \omega_{\xi j} b_{\xi j}^\dagger b_{\xi j}. \tag{6}
\]

Oscillators are labeled by site index \( j \) and mode index \( \xi \) and phonon creation. The annihilation operators \( b_{\xi j}^\dagger \) and \( b_{\xi j} \) satisfy Bose commutation relations. The interaction of electronic excitations of the aggregate with the environment is taken to be linear in mode displacements and local to each chromophore (Holstein-like coupling \cite{47})

\[
H_{M-B} = \sum_j |B_j^\dagger B_j| u_j, \tag{7}
\]

where the collective environment coordinate \( u_j \) associated with chromophore \( j \) reads as

\[
u_j = \sum_{\xi} g_{j\xi} \left( b_{j\xi}^\dagger + b_{j\xi} \right). \tag{8}
\]

We assume that the sets of environmental modes are the same on each site, i.e., mode frequencies \( \omega_{\xi} \) do not depend on site index. Coupling constants \( g_{j\xi} \) depend on site index \( j \), and may be related to the displacement of the equilibrium configuration of mode \( \xi \) between the ground and excited electronic state of chromophore \( j \) \cite{43,44}.

The coupling between aggregate excitations and the radiation is taken in the dipole and rotating wave approximations

\[
H_{M-R} = -\mu_{eg} \cdot \mathbf{E}^{(+)} - \mu_{ge} \cdot \mathbf{E}^{(-)}. \tag{9}
\]

The dipole-moment operator \( \mu \) is assumed to be a purely electronic operator

\[
\mu = \sum_j d_j \left( B_j^\dagger + B_j \right) = \mu_{eg} + \mu_{ge}, \tag{10}
\]

where transition dipole moment \( d_j \) of chromophore \( j \) does not depend on environmental coordinates (Condon approximation), part \( \mu_{eg} \) contains only operators \( B_j^\dagger \) and \( B_j \), and \( \mu_{ge} \) contains only operators \( B_j \). \( \mathbf{E}^{(+)} \) denotes the positive- and negative-frequency parts of the (time-independent) operator of the (transversal) electric field, so that we treat both electronic excitations and the radiation generating them on quantum level.

We assume that, at the initial instant \( t_0 \) of our dynamics, the total statistical operator \( W(t_0) \) representing the state of the combined system of aggregate excitations, environment, and radiation, can be factorized as follows

\[
W(t_0) = |0\rangle \langle 0| \otimes \rho_B^0 \otimes \rho_R. \tag{11}
\]

In Eq. (11), the aggregate is taken to be initially unexcited, the state of the environment \( \rho_B^0 \) is adapted to the electronic ground state of the aggregate (\( T = (k_B T)^{-1} \) is the temperature),

\[
\rho_B^0 = \frac{\exp(-\beta H_B)}{\text{Tr}_B \exp(-\beta H_B)}, \tag{12}
\]

while \( \rho_R \) describes the state of the radiation.

Should we want to restore the light–matter interaction in its semiclassical form, it is enough to formally replace electric-field operator \( \mathbf{E}^{(\pm)} \) in Eq. (9) by a time-dependent vector \( \mathbf{E}^{(\pm)}(t) \), which then enters all equations as a classical parameter. As our further discussion will show, in that case, \( \mathbf{E}^{(\pm)}(t) = \mathbf{T}_R \left\{ \mathbf{E}^{(\pm)}(t) \rho_R \right\} \), where \( \mathbf{E}^{(\pm)}(t) \) is the electric-field operator in the Heisenberg picture.
III. EQUATIONS OF MOTION: SEMICLASSICAL TREATMENT OF LIGHT–MATTER INTERACTION

The excitation with an arbitrary time-dependent (classical) electric field $\mathcal{E}(t)$ can be incorporated into HEOM formalism by augmenting Hamiltonian $H_M$ by the purely electronic and time-dependent Hamiltonian $H_{M-R}(t)$ [25, 26]. Indeed, all the steps in the derivation conducted in Ref. [48] can be repeated to obtain equations of motion for the reduced DM (RDM) $\rho(t) \equiv \sigma_0(t)$ and auxiliary DMs (ADMs) $\sigma_n(t)$. ADMs are fully specified by vector $n$ of non-negative integers $n_{j,m}$.

$$n = \left\{ (n_{1,0}, n_{1,1}, \ldots), \ldots, (n_{N,0}, n_{N,1}, \ldots) \right\}. \quad (13)$$

The index $j = 1, \ldots, N$ enumerates chromophores, while index $m$, in principle, does not have an upper limit and is related to the following expansion of the bath correlation function in terms of exponentially decaying factors ($t > 0$)

$$C_j(t) = \text{Tr}_B \left\{ u_j^{(f)}(t) u_j(0) \rho^g_B \right\} = \sum_m c_{j,m} e^{-\mu_j \cdot m \cdot t}. \quad (14)$$

The time dependence of the collective coordinate $u_j^{(f)}(t)$ in Eq. (14) is with respect to the free-phonon Hamiltonian, Eq. (6). While expansion coefficients $c_{j,m}$ may be complex, the decay rates $\mu_j$ are assumed to be real and positive. We note that, apart from the exponential decomposition scheme [Eq. (14)] adopted in this work, there are other decompositions of $C_j(t)$ from which a HEOM approach may be derived [49]. The bath correlation function is commonly expressed in terms of the so-called spectral density $J_j(\omega)$,

$$C_j(t) = \frac{\hbar}{\pi} \int_0^{+\infty} d\omega J_j(\omega) \times \left[ \coth \left( \frac{\beta\hbar\omega}{2} \right) \cos(\omega t) - i \sin(\omega t) \right], \quad (15)$$

which conveniently combines information on the density of environmental-mode states and the respective coupling strengths to electronic excitations [43, 44].

The equation of motion for ADM $\sigma_n(t)$ reads as [48]

$$\partial_t \sigma_n(t) = -\frac{i}{\hbar} [H_M, \sigma_n(t)] + \frac{1}{\hbar} \left[ \mu_{eg} \mathcal{E}^{(+)}(t) + \mu_{ge} \mathcal{E}^{(-)}(t), \sigma_n(t) \right]$$

$$- \left( \sum_j \sum_m n_{j,m} \mu_{j,m} \right) \sigma_n(t) + i \sum_j \sum_m \left[ V_j, \sigma_{n_j,m}^+(t) \right]$$

$$+ i \sum_j \sum_m n_{j,m} \left( \frac{c_{j,m}}{\hbar^2} V_j \sigma_{n_j,m}^+(t) - \frac{c_{j,m}^*}{\hbar^2} \sigma_{n_j,m}(t) V_j \right), \quad (16)$$

where $V_j = B_j^\dagger B_j$. Let us note that, since the coupling to the radiation is explicitly included in the electronic Hamiltonian, HEOM treats nonperturbatively not only the interaction with bath, as usually, but also that with light. Bearing in mind that our formulation of the model Hamiltonian supports states with arbitrary number of excitations, the result embodied in Eq. (16) is quite general. In principle, it can describe in great detail a nonlinear spectroscopy experiment of an arbitrary order. However, once we fix the highest order in the electric field we are interested in, there will be many elements of DMs that do not contribute to the optical response up to that order. In other words, solving coupled equations (16) as they stand, we obtain much more information than necessary to reconstruct the optical response up to a given order. Moreover, we lack the intuitive physical picture characteristic of nonlinear spectroscopy, which is in terms of Liouville pathways, block structure of the statistical operator and evolution superoperator, etc [17, 23]. In order to circumvent these deficiencies, it is enough to make projection of the dynamics on relevant excitonic subspaces. For example, in the third-order spectroscopy experiment, it would be enough to consider subspaces that can accommodate up to two excitations, i.e., to reduce the dynamics given in Eq. (16) to the direct sum $H_0 \oplus H_1 \oplus H_2$ [23]. Similarly, the second-order response is fully characterized by the reduction to $H_0 \oplus H_1$. This is demonstrated in greater detail further in this section and in Sec. I of Ref. [51] (Supplemental Material to this manuscript). Practically, the reduction to $H_0 \oplus H_1$ is achieved by performing the following replacements

$$B_j \rightarrow |g\rangle \langle j|, \quad B_j^\dagger \rightarrow |j\rangle \langle g|, \quad B_k \rightarrow |j\rangle \langle k| \quad (17)$$

in the model Hamiltonian.

Therefore, to obtain the second-order response, we should calculate the expectation values $n_{g,n}(t) \equiv \langle g| \sigma_n(t) |g\rangle$, $y_{e,n}(t) \equiv \langle e| \sigma_n(t) |g\rangle$ and $n_{ee,n}(t) \equiv \langle e| \sigma_n(t) |e\rangle$, where $\{|e\rangle\}$ is an arbitrary basis in $H_1$ (the notation is similar to that in Ref. [29]). If $n = 0$, these three expectation values respectively represent the ground-state population, optical coherences, and singly excited-state populations and intraband coherences. Since the electronic subsystem starts from $|g\rangle \langle g|$, and since the light–matter coupling $H_{M-R}$ is the only part of the Hamiltonian that can cause transitions from the ground state to singly excited states, the following relations hold [51]

$$n_{g,n}(t) = \delta_{n,0} + \sum_{k=1}^{+\infty} n_{g,k}(t), \quad n_{g,k}(t) \propto \mathcal{E}^{2k}, \quad (18a)$$

$$y_{e,n}(t) = \sum_{k=0}^{+\infty} y_{e,k+1}(t), \quad y_{e,k+1}(t) \propto \mathcal{E}^{2k+1}, \quad (18b)$$

$$n_{ee,n}(t) = \sum_{k=1}^{+\infty} n_{ee,k}(t), \quad n_{ee,k}(t) \propto \mathcal{E}^{2k}. \quad (18c)$$

In other words, optical coherences are dominantly linear in the applied field, while exciton populations are at least
quadratic in the applied field. The environmental assistance, which actually enters through vector $n$ \[32\], does not affect the scaling laws \[18\].

Formulating equations of motion for $y_{n}(t)$ and $v_{n}(t)$ actually enables us to formulate operator equations for sectors $e$ and $ee$ of $\sigma_{n}(t)$. Namely, using Eqs. \[15\] and keeping only terms that are at most of the second order in the applied field, we form the following equations for the $e$ sector $\sigma_{eg,n}(t)$ and for the $ee$ sector $\sigma_{ee,n}(t)$

$$\partial_t \sigma_{eg,n}(t) = -\frac{i}{\hbar} [H_{M}, \sigma_{eg,n}(t)] - \left( \sum_{j} \sum_{m} n_{j,m} \mu_{j,m} \right) \sigma_{eg,n}(t) + \frac{\delta_{n,0}}{\hbar} \mathcal{E}(t) \mu_{eg} + i \sum_{j} \sum_{m} V_{j} \sigma_{eg,n_{j,m}}^{+}(t) + i \sum_{j} \sum_{m} n_{j,m} \frac{c_{j,m}}{\hbar^2} V_{j} \sigma_{eg,n_{j,m}}^{-}(t), \quad (19)$$

$$\partial_t \sigma_{ee,n}(t) = -\frac{i}{\hbar} [H_{M}, \sigma_{ee,n}(t)] - \left( \sum_{j} \sum_{m} n_{j,m} \mu_{j,m} \right) \sigma_{ee,n}(t) + \frac{i}{\hbar} \mathcal{E}(t) \mu_{eg} \sigma_{eg,n}(t) - \frac{i}{\hbar} \sigma_{ee,n}(t) \mu_{ee} \mathcal{E}(t) \mu_{ee} \sigma_{eg,n}(t) + i \sum_{j} \sum_{m} \left[ V_{j}, \sigma_{ee,n_{j,m}}^{+}(t) \right] \sigma_{ee,n_{j,m}}^{-}(t) + i \sum_{j} \sum_{m} n_{j,m} \frac{c_{j,m}}{\hbar^2} V_{j} \sigma_{ee,n_{j,m}}^{-}(t) - i \sum_{j} \sum_{m} n_{j,m} \frac{c_{j,m}}{\hbar^2} \sigma_{ee,n_{j,m}}^{+}(t) V_{j}, \quad (20)$$

where now $V_{j} \rightarrow |j\rangle\langle j|$. By reducing our dynamics to the subspaces containing at most one excitation, we transform Eq. \[10\] into coupled equations describing evolution of optical coherences \[19\] and excited-state populations and intraband coherences \[20\]. The crucial step in the transformation is the application of scaling laws in Eqs. \[18\], which ensure that our dynamics is consistently up to the second order in the exciting field.

Instead of the path we have taken, one could have started from the model Hamiltonian in which the replacements of Eq. \[17\] are performed, and solved Eq. \[16\] without even considering the scaling laws in Eqs. \[18\]. In that case, one would in principle obtain the solution that is exact to all orders in the exciting field. However, this exactness is only apparent, because the proper treatment of higher orders in the exciting field requires enlarging the space on which the Hamiltonian is formulated, as we demonstrate in more detail in Sec. I of Ref. \[50\] (Supplemental Material to this manuscript). Temporal evolutions of higher-order sectors of the density matrix (which are not taken into account) would then influence evolutions of optical coherences, excited-state populations, and intraband coherences. For example, as demonstrated in Ref. \[29\], already in the third order in the electric field, equations of motion for optical coherences are coupled to equations of motion for biexcitonic amplitudes (coherences between the ground state and doubly excited states), meaning that a separate equation governing the evolution of $|jk\rangle\langle gj|$ block of $\sigma_{n}(t)$ has to be formulated. This discussion emphasizes that, once we treat the photon-generation step explicitly, we should be aware of the close connection between the largest order in the exciting field we include and the space on which the dynamics has to be formulated. Should we limit ourselves to the Frenkel Hamiltonian for the singly excited states and, at the same time, explicitly describe the excitation generation by light, we should do that only up to the second order in the applied field.

Let us conclude this section by noting that the results we have presented so far heavily rely on the form of the light–matter interaction Hamiltonian in the semiclassical approximation. If we want to treat light quantum mechanically, too, results of Ref. \[21\] suggest that, up to the second order in the exciting field, the only information we need about light is its first-order (two-point) correlation function (indices $i, j$ label Cartesian components of a vector)

$$G_{ij}^{(1)}(\tau_{2}, \tau_{1}) = \text{Tr}_{R} \left\{ \left\{ \mathbf{E}^{(+)}(\tau_{2}) \right\} \left\{ \mathbf{E}^{(+)}(\tau_{1}) \right\} \right\}_{i} \rho_{R}, \quad (21)$$

In developments presented up to now, such a quantity does not directly enter Eqs. \[16\], \[19\], and \[20\]. However, for (classical, transform-limited) pulses, this correlation function factorizes into products of expectation values of single-electric-field operators, which define classical values of the electric field \[53\] \[55\].

$$G_{ij}^{(1)}(\tau_{2}, \tau_{1}) = \mathcal{E}_{i}^{(-)}(\tau_{2}) \mathcal{E}_{j}^{(+)}(\tau_{1}), \quad (22a)$$

$$\mathcal{E}_{i}^{(\pm)}(\tau) = \text{Tr}_{R} \left\{ \left\{ \mathbf{E}^{(\mp)}(\tau) \right\} \right\}_{i} \rho_{R}, \quad (22b)$$

As will be demonstrated in more detail in Sec. \[16\] it is precisely this factorization that enables us to formulate Eqs. \[16\] and \[20\] as they stand. On fairly general grounds, since $G_{ij}^{(1)}(\tau_{2}, \tau_{1})$ is a two-particle quantity \[56\], it can always be expressed as the product of two single-particle quantities \[22\] plus the correlated two-particle reminder. While the factorization of $G_{ij}^{(1)}(\tau_{2}, \tau_{1})$ into a product of two single-particle quantities reflects the classical aspects of the radiation state, the remaining two-particle correlation has no classical counterpart, i.e., it captures genuinely quantum aspects of the radiation state. In the following sections, we obtain a formally exact result that enables us to consistently treat the second-order excitonic dynamics triggered by light of arbitrary
properties along with a nonperturbative treatment of the excitation–environment coupling.

IV. GENERAL THEORY OF SECOND-ORDER LIGHT-INDUCED DYNAMICS

In the interaction picture, the total DM $W^{(I)}(t)$ of the combined system comprising the molecular aggregate, its environment, and the radiation field, evolves according to

$$\partial_t W^{(I)}(t) = -\frac{i}{\hbar} \left[ H_{M-B}^{(I)}(t) + H_{M-R}^{(I)}(t), W^{(I)}(t) \right],$$  \hspace{1cm} (23)

$$W^{(I)}(t) = \sum_{n=0}^{+\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^t \! \! dt_1 \cdots \int_{t_0}^{t_2} \! \! dt_1 \left[ H_{M-B}^{(I)}(\tau_{n-1}) + H_{M-R}^{(I)}(\tau_{n-1}), \cdots, H_{M-B}^{(I)}(\tau_{1}) + H_{M-R}^{(I)}(\tau_{1}), W(t_0) \right] \cdots .$$  \hspace{1cm} (26)

Let us now focus on the case of weak interaction with the radiation by keeping in Eq. (26) only contributions that contain no more than two interaction Hamiltonians $H_{M-R}$. At the same time, as discussed in Sec. III, this means that we can safely reduce our description to $\mathcal{H}_0 \oplus \mathcal{H}_1$ and consequently make the replacements embodied in Eq. (17) in the model Hamiltonian. The specific form of the initial condition [Eq. (11)], as well as the fact that any nontrivial dynamics is ultimately induced by $H_{M-R}$, enable us to separately treat different electronic sectors ($gg$, $eg$, and $ee$) of the total DM. By electronic sectors $gg$, $eg$, and $ee$ of the total DM, we understand here its parts that, after appropriate reductions, contain information on the ground-state population, optical coherences, and excited-state populations and intraband coherences, respectively. After a straightforward analysis, we obtain the following results for the $eg$ sector

$$W_{eg}^{(I)}(t) = -\frac{i}{\hbar} \int_{t_0}^t \! \! dt \ U_{M-B}^{(I)}(t, \tau) H_{M-R}^{(I)}(\tau) W(t_0),$$  \hspace{1cm} (27)

for the $gg$ sector

$$W_{gg}^{(I)}(t) = W(t_0) - \frac{i}{\hbar} \int_{t_0}^t \! \! dt \ H_{M-R}^{(I)}(\tau) W_{eg}^{(I)}(\tau) + \frac{i}{\hbar} \int_{t_0}^t \! \! dt \ W_{eg}^{(I)}(\tau) H_{M-R}^{(I)}(\tau),$$  \hspace{1cm} (28)

and for the $ee$ sector

$$W_{ee}^{(I)}(t) = \int_{t_0}^t \! \! dt_2 \int_{t_0}^{t_2} \! \! dt_1 U_{M-B}^{(I)}(t_2, t_1) U_{M-B}^{(I)}(\tau_2, \tau_1) \left( \frac{1}{\hbar^2} H_{M-R}^{(I)}(\tau_1) W(t_0) H_{M-R}^{(I)}(\tau_2) \right) U_{M-B}^{(I)}(t_2, t_1)$$

$$\quad + \int_{t_0}^t \! \! dt_2 \int_{t_0}^{t_2} \! \! dt_1 U_{M-B}^{(I)}(t_2, t_1) \left( \frac{1}{\hbar^2} H_{M-R}^{(I)}(\tau_2) W(t_0) H_{M-R}^{(I)}(\tau_1) \right) U_{M-B}^{(I)}(t_2, t_1).$$  \hspace{1cm} (29)

In Eqs. (27) and (29),

$$U_{M-B}^{(I)}(s_2, s_1) = T \exp \left[ -\frac{i}{\hbar} \int_{s_1}^{s_2} ds H_{M-B}^{(I)}(s) \right],$$  \hspace{1cm} (30)

where $T$ denotes the chronological time ordering. The result embodied in Eq. (29) can be interpreted in terms of double-sided Feynman diagrams [17]. The two summands represent the two Liouville pathways from $|g\rangle\langle g|$ to $|e\rangle\langle e|$, which differ by the time order of the interactions with the bra and ket. These two summands are complex conjugates of one another, so that $W_{ee}^{(I)}(t)$ is a Hermitian operator [27]. Therefore, in further discussions, it will be enough to perform manipulations with the first summand only.

Let us note that the total number of excitations, which is given by the (total) trace of $W(t)$ [or $W^{(I)}(t)$], is conserved. This is most easily proven by rewriting Eqs. (29) and (28) as differential equations.
The RDM containing excited-state populations and intraband coherences is obtained by performing partial traces with respect to the radiation and the thermal bath

$$\rho_{ee}^{(I)}(t) = \text{Tr}_B \left\{ \text{Tr}_R \left\{ W_{ee}^{(I)}(t) \right\} \right\}.$$  \hspace{1cm} (31)

Let us concentrate on reducing the first term in Eq. (29). The partial trace over radiation is computed straightforwardly, since radiation operators enter Eq. (29) only through the two $H_{M-R}$ terms. In more detail,

$$\frac{1}{\hbar^2} \text{Tr}_R \left\{ H_{M-R}^{(I)}(\tau_1) W(t_0) H_{M-R}^{(I)}(\tau_2) \right\} = A^{(I)}(\tau_2, \tau_1) \rho_B^q,$$

where the purely electronic operator $A^{(I)}(\tau_2, \tau_1)$ is defined as

$$A^{(I)}(\tau_2, \tau_1) = \frac{1}{\hbar^2} \sum_{i,j} G_{ij}^{(I)}(\tau_2, \tau_1) \times \left\{ \mu_{eg}(\tau_1) \right\}_i |g \rangle \langle g | \left\{ \mu_{ge}(\tau_2) \right\}_j.$$

In Eq. (32), the sums over $i$ and $j$ are performed over Cartesian components of the electric field, whereas $G_{ij}^{(I)}(\tau_2, \tau_1)$ is defined in Eq. (21). Therefore, in the limit of weak aggregate–radiation interaction, the radiation enters the reduced dynamics of excited-state populations and intraband coherences only via its first-order correlation function, as has already been demonstrated [20]. Integrating over the bath degrees of freedom provides us with the second ingredient governing the excitonic dynamics, which is the reduced evolution superoperator explicitly containing the two interaction instants $\tau_1$ and $\tau_2$ with the radiation, as well as the observation instant $t$. Having taken partial trace over radiation, we now expand each phonon propagator [Eq. (25)] entering Eq. (29) in powers of $H_{M-B}$. Since the averaging is performed over the canonical density matrix of the bath [Eq. (12)], Wick’s theorem ensures that only contributions containing an even number of $H_{M-B}$ operators should be evaluated and that the final result is entirely expressed in terms of the two-point (noninteracting) bath correlation function $C(j \mid t)$ defined in Eq. (11) [57, 58].

The procedure is described in greater detail in Sec. II of Ref. 57 (Supplemental Material to this manuscript). Finally, the reduced excited-state density matrix reads as

$$\rho_{ee}^{(I)}(t) = \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \overline{U}_{\text{red}}^{(I)}(t, \tau_2, \tau_1) A^{(I)}(\tau_2, \tau_1) +$$

$$+ \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 A^{(I)}(\tau_2, \tau_1) \overline{U}_{\text{red}}^{(I)}(t, \tau_2, \tau_1).$$

(34)

The arrow above the propagator sign indicates the direction of its action on the corresponding operator. The reduced propagator acting on the right reads as

$$\overline{U}_{\text{red}}^{(I)}(t, \tau_2, \tau_1) = T \exp \left[ \overline{W}_c(\tau_2, \tau_1) + \overline{W}_p(t, \tau_2) + \overline{W}_{c-p}(t, \tau_2, \tau_1) \right],$$

$$\overline{W}_c(\tau_2, \tau_1) = -\frac{1}{\hbar^2} \sum_{j} \int_{\tau_1}^{\tau_2} d\tau_2 \int_{\tau_2}^{\tau_2} d\tau_1 V_j^{(I)}(s_2) \times C_j(s_2 - s_1) V_j^{(I)}(s_1) \times C,$$

$$\overline{W}_p(t, \tau_2) = -\frac{1}{\hbar^2} \sum_{j} \int_{\tau_2}^{\tau} d\tau_2 \int_{\tau_2}^{\tau_2} d\tau_1 V_j^{(I)}(s_2) \times \left( C_j^{\ast}(s_2 - s_1) V_j^{(I)}(s_1) \times + i C_j(s_2 - s_1) V_j^{(I)}(s_1) \right),$$

$$\overline{W}_{c-p}(t, \tau_2, \tau_1) = -\frac{1}{\hbar^2} \sum_{j} \int_{t}^{\tau_2} d\tau_2 \int_{\tau_2}^{\tau_2} d\tau_1 V_j^{(I)}(s_2) \times C_j(s_2 - s_1) V_j^{(I)}(s_1) \times C.$$

(35a)

In Eq. (35c), $C_j^{\ast}$ denote the real and imaginary part of the two-point bath correlation function $C_j$ [Eq. (11)], whereas the action of hyperoperators $V_j^{\ast, \circ, \ast, C_j}$ on an operator $O$ is defined as

$$V_j^{\ast} O = [V_j, O],$$

$$V_j^{\circ} O = \{V_j, O\},$$

$$V_j^{C} O = V_j O.$$

(36a)

(36b)

(36c)

A similar expression holds for the propagator acting on the left, as detailed in Sec. II of Ref. 57 (Supplemental Material to this manuscript).

Equations (31) and (35) are the main results of our analysis. They present an exact solution (with respect to the aggregate–environment coupling) of the dynamics of an excitonic system weakly driven by light of arbitrary properties. The principal novelty compared to a similar analysis conducted in Refs. 20 and 21 is that, here, we provide an exact expression for the reduced evolution superoperator that is compatible with the interaction with light, i.e., it explicitly depends on the interaction instants with the radiation and the observation instant.

The RDM evolution can be conveniently represented in terms of diagrams showing how the state of electronic excitations changes due to interactions with radiation and due to absorptions and emissions of elementary en-
FIG. 1. Primitive diagrams describing the changes that the state of electronic excitations undergoes due to the interaction with the radiation and environment-assisted processes. Only the diagrams characteristic for the first-order approximation to the reduced propagator [Eq. (35a)] in the first term of Eq. (34) are presented. The instants \( \tau_1 \) and \( \tau_2 \) at which the electronic system interacts with light, as well as the instants \( s_1 \) and \( s_2 \) determining the environmental assistance, are fixed. The arrows at \( \tau_1 \) and \( \tau_2 \) depict interactions with light, which are reflected in changes in the ket and bra of RDM. Circumferences represent the bath correlation function \( C_j(s_2 - s_1) \). The observation time \( t \) satisfies \( t \geq \tau_2 \geq \tau_1 \geq t_0 \). Diagram (a) corresponds to Eq. (35a), diagram (b) corresponds to Eq. (35b), and diagram (c) corresponds to Eq. (35c).

In this discussion, we assume that the instants \( \tau_1 \) and \( \tau_2 \) at which the interactions with the radiation occur are fixed. We further focus on the first-order term of the reduced evolution superoperator [Eq. (35a)] and we also fix instants \( s_1 \) and \( s_2 \) [Eqs. (35b)–(35d)] that describe a single environmentally assisted process. In Figs. 1(a), 1(b), and 1(c) we present the three primitive diagrams corresponding to the hyperoperators in Eqs. (35a)–(35c), respectively. The diagram in Fig. 1(a) describes a single-phonon-assisted process during which the electronic subsystem is in a state of optical coherence. The diagram in Fig. 1(b) describes a single-phonon-assisted process during which the electronic subsystem is entirely in the excited-state manifold. The single-phonon-assisted process represented by the primitive diagram in Fig. 1(c) starts when the electronic subsystem is in a state of optical coherence, and ends when it is entirely in the excited-state manifold. There, the phonon propagator straddles two temporal sectors defined by the interactions with the radiation. These so-called straddling evolutions [59, 60] fully capture the nonequilibrium dynamics of the bath during different periods of photoinduced evolution [26]. They are intimately connected to the quantum coherence between electronic excitations and environment and their presence is crucial to accurately describe photoinduced electronic dynamics.

Let us point out another viewpoint on the result embodied in Eq. (34). Equation (34) can be formally rewritten by introducing the dipole-moment hyperoperators that act the initial electronic state |\( g \rangle \langle g |\) from the opposite sides

\[
A^{(f)}(\tau_2, \tau_1) = \frac{1}{\hbar^2} \sum_{i,j} G^{(1)}_{ij}(\tau_2, \tau_1) \times 
C \left\{ \mu^{(f)}_{g^c}(\tau_2) \right\}_i \left\{ \mu^{(f)}_{e^g}(\tau_1) \right\}_j |g\rangle \langle g |.
\]

where we introduced hyperoperator \( C^V \) as \( C^V O = OV \), for any operators \( V \) and \( O \). Then, Eq. (34) can be interpreted in terms of a sequence of hyperoperators \( V^{\times,o,C} \), \( C^\mu \), and \( C^\circ \mu \) acting on the initial state of the electronic subsystem \(|g\rangle \langle g |\). The derivation of the reduced evolution superoperator produced a global time-ordering sign in front of the exponential. Apparently, this global \( T \) sign is in no manner connected to \( A^{(f)}(\tau_2, \tau_1) \). However, analyzing the reduced propagator term by term and order by order, we see that the temporal order of hyperoperators \( V^{\times,o,C} \) in each term is compatible with the temporal order in which hyperoperators \( \mu^C \) and \( C^\circ \mu \) in Eq. (34) act on \(|g\rangle \langle g |\). Namely, the hyperoperator \( V^C \) in Eqs. (35a) and (35b) acts after change of the electronic state by the first interaction with radiation and before the next change of the electronic state. Similarly, hyperoperators \( V_j^{\times,o} \) in Eqs. (35a) and (35b) act only after both interactions with radiation. Therefore, we can introduce one global \( T \) sign and formally rewrite Eq. (34) as

\[
\rho^{(f)}_{ee}(t) = \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \frac{1}{\hbar^2} \sum_{i,j} G^{(1)}_{ij}(\tau_2, \tau_1) \times 
T \left\{ \exp \left[ \hat{W}_c(\tau_2, \tau_1) + \hat{W}_p(t, \tau_2) + \hat{W}_c-p(t, \tau_2, \tau_1) \right] \right\}_C \left\{ \mu^{(f)}_{g^c}(\tau_2) \right\}_i \left\{ \mu^{(f)}_{e^g}(\tau_1) \right\}_j |g\rangle \langle g | + H.c.
\]

This viewpoint will be useful in our discussion in Sec. V C, where we emphasize the similarities between the descriptions of the second-order photoexcitation process starting from the ground state and the Förster energy transfer from an excited donor to an unexcited acceptor.

Even though the result embodied in Eqs. (34) and (35a) is remarkable, it is not very useful for actual
computations, principally due to the time-ordering sign that renders analytical manipulations difficult. Nevertheless, whenever the bath correlation function $C_j(t)$ can be represented in the form given in Eq. (14), Eqs. (34) and (35) can be recast as an infinite hierarchy of equations of motion for RDM and ADMs [18]. However, the details of this procedure now depend on the form of operator $A^{(I)}(\tau_2, \tau_1)$ [Eq. (33)], i.e., on the temporal and statistical properties of the radiation.

V. EXCITATION BY WEAK (COHERENT) LASER PULSES

As has been recently discussed in Refs. [54] and [55], a pulse of light may be understood as a classical-like state of the electromagnetic field, whose energy density is localized and which can be specified by the spatial position around which it is localized, propagation direction, polarization, and spectral distribution. In essence, the quantum state representing the classical pulse whose bandwidth is determined by its spectral distribution is a coherent state which, as first realized by Glauber [53], factorizes the $2n$-point radiation correlation function into product of $2n$ expectation values of the electric-field operator. In particular, $G^{(I)}_{ij}(\tau_2, \tau_1)$ is then factorized as predicted by Eq. (22), so that $A^{(I)}(\tau_2, \tau_1)$ [Eq. (33)] assumes the form

$$A^{(I)}(\tau_2, \tau_1) = \frac{1}{\hbar^2} \left[ \mu^{(I)}_{eg}(\tau_1) \cdot \mathcal{E}^{(+)}(\tau_1) \right] |g\rangle\langle g| \times \left[ \mu^{(I)}_{ge}(\tau_2) \cdot \mathcal{E}^{(-)}(\tau_2) \right]. \tag{39}$$

The manipulations that are necessary to recast Eqs. (40) and (34) as HEOM presented in Eqs. (19) and (20), respectively, proceed as usually [18]. Here, we only present the definitions of ADMs (in the interaction picture) for optical coherences

$$\sigma^{(I)}_{eg, n}(t) = \int_{t_0}^{t} d\tau T \left\{ \prod_j \prod_m \left[ \int_{\tau}^{t} ds \ e^{-\mu_j, m(t-s)} \frac{c_{j, m}}{\hbar^2} V_j^{(I)}(s) \right]^{n_{j, m}} U^{(I)}_{\text{red}}(t, \tau) \right\} \frac{i}{\hbar} \mu^{(I)}_{eg}(\tau) \mathcal{E}^{(+)}(\tau) |g\rangle\langle g|, \tag{42}$$

and for excited-state populations and intraband coherences ($c_{j, m}^{r/i}$ denote the real/imaginary part of complex coefficients $c_{j, m}$)

$$\sigma^{(I)}_{ee, n}(t) = \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 T \left\{ \prod_j \prod_m \left[ \int_{\tau_1}^{\tau_2} ds \ e^{-\mu_j, m(t-s)} \left( \frac{c_{j, m}^{r}}{\hbar^2} V_j^{(I)}(s) \times - \frac{c_{j, m}^{i}}{\hbar^2} V_j^{(I)}(s)^{\circ} \right) + \int_{\tau_1}^{\tau_2} ds \ e^{-\mu_j, m(t-s)} \frac{c_{j, m}}{\hbar^2} V_j^{(I)}(s)^{\circ} \right]^{n_{j, m}} U^{(I)}_{\text{red}}(t, \tau_2, \tau_1) \right\} A^{(I)}(\tau_2, \tau_1) + \text{H.c.} \tag{43}$$

Before discussing the relation of the HEOM embodied in Eqs. (19) and (20) to existing theories of the dynamics of photoinduced electronic excitations, let us briefly comment on the way in which the photoexcitation enters the HEOM. The electric field explicitly enters the hierarchy for optical coherences only on the level of RDM, see Eq. (19). Environmentally assisted optical coherences then act as source terms for environmentally assisted excited-state populations and intraband coherences, see Eq. (20). Moreover, the source term for the $ee$ sector of
ADM characterized by vector \( \mathbf{n} \) comprises only the \( e \ g \) sector of ADM characterized by the same vector \( \mathbf{n} \). The hierarchy is schematically presented in Fig. 2 for \( N = 2 \) chromophores and \( K = 1 \) term in the decomposition of the bath correlation function \( C_j(t) \) in Eq. (13).

\[
D = 0 \\
D = 1 \\
D = 2
\]

FIG. 2. Schematic representation of the HEOM for optical coherences and excited-state populations and intraband coherences in the case of excitation by a weak laser pulse. For the sake of simplicity, the aggregate comprises \( N = 2 \) chromophores and only \( K = 1 \) term in the exponential decomposition of the bath correlation function \( C_j(t) \) is taken into account. Individual DMs are represented by circles, while the driving by the electric field \( \mathcal{E}(t) \), which directly affects only the optical-coherence RDM, is presented by the straight horizontal arrow. \( D \) denotes the level of the hierarchy, and each DM is accompanied by the corresponding vector \( \mathbf{n} \), see Eq. (18). Curved dashed arrows represent hierarchical links between optical-coherence DMs, while curved solid arrows represent hierarchical links between excited-state DMs. The fact that \( \sigma_{e, e, n}(t) \) acts as the source term in the EOM for \( \sigma_{e, e, n}(t) \) is reflected in the diagram by the presence of curved dash-dotted arrows pointing from \( \sigma_{e, e, n}(t) \) towards \( \sigma_{e, e, n}(t) \).

A. Impulsive Photoexcitation of Pure-Dephasing Spin–Boson Model: Analytical Results

Let us now concentrate on the case of only one chromophore. The Hamiltonian, Eq. (11), then reads as

\[
\begin{align*}
H &= \varepsilon_e |e\rangle\langle e| + \sum_{\xi} \hbar \omega_{\xi} b_{\xi}^\dagger b_{\xi} \\
&\quad + \sum_{\xi} g_{\xi} |e\rangle\langle e| \left( b_{\xi}^\dagger + b_{\xi} \right) \\
&\quad - d_{eg} \cdot \left( \mathcal{E}^{(+)}(t) |e\rangle\langle g| + \mathcal{E}^{(-)}(t) |g\rangle\langle e| \right).
\end{align*}
\]

(44)

Remembering that we set the ground-state energy as zero of our energy scale, we conclude that the Hamiltonian in Eq. (11) is actually the pure-dephasing spin–boson Hamiltonian (or the independent-boson Hamiltonian, see Ref. [57]), in which \( \varepsilon_e \) is the energy splitting between the two local energy levels (the ground state \( |g\rangle \) and the singly excited state \( |e\rangle \)), and there is no tunneling between the two levels. The hyperoperators appearing in the reduced evolution superoperator are time-independent, meaning that the time-ordering signs are not effective. This circumstance enables us to obtain analytical insights into the photoexcitation dynamics of the pure-dephasing spin–boson model in the impulsive limit.

The waveform of the positive-frequency part of the electric field is taken to be

\[
\mathcal{E}^{(+)}(t) = e^0 \delta(t) e^{-i\Omega_p t},
\]

(45)

where vector \( e \) defines the polarization of the pulse, \( \Omega_p \) is its central frequency, and \( \mathcal{E}_0 \) is its amplitude. If the initial instant is \( t_0 < 0 \), the excited-state RDM for \( t > 0 \) reads as

\[
\rho_{ee}(t) = \frac{1}{\hbar^2} \langle \mathbf{d}_{eg} \cdot e \rangle \mathcal{E}_0^2 |e\rangle\langle e| \equiv P_e |e\rangle\langle e|.
\]

(46)

The crucial step to obtain Eq. (46) is to note that, in the impulsive limit, both interactions with the radiation occur at \( \tau_2 = \tau_1 = 0 \), so that \( \mathcal{W}_{ie}(\tau_2, \tau_1) \) [Eq. (35a)] and \( \mathcal{W}_{ie\rightarrow p}(\tau_2, \tau_1) \) [Eq. (35c)] are equal to zero. Hyperoperator \( \mathcal{W}_{ie}(\tau_2, \tau_1) \) [Eq. (35d)] also effectively reduces to zero, because it eventually acts as the commutator \( [e]|e\rangle\langle e| \). At the same time, the optical-coherence RDM

\[
\rho_{ee}(t) = \frac{1}{\hbar^2} \langle \mathbf{d}_{eg} \cdot e \rangle \mathcal{E}_0 e^{-i\varepsilon_e t/\hbar} e^{-g(t)} |e\rangle\langle g|.
\]

(47)

exponentially decays to zero on a time scale determined by the temporal behavior of the lineshape function

\[
g(t) = \frac{1}{\hbar^2} \int_0^t ds_2 \int_0^{s_2} d\Omega C(\Omega).
\]

(48)

In a certain sense, Eqs. (46) and (47) formally demonstrate that the propagation scheme adopted in, e.g., Ref. [48], is physically sensible. Namely, optical coherences generated upon impulsive photoexcitation quickly decay to zero and, more importantly, they do not act as sources for excited-state populations and intraband coherences for \( t > 0 \), see Eqs. (15–17). Therefore, upon a delta-like photoexcitation, it is justified to propagate only the excited-state dynamics. The reduced propagator for the excited-state sector, Eq. (43), then becomes the reduced propagator used in Ref. [48].

Although the excited-state RDM does not evolve in time, the impulsive photoexcitation triggers environmental reorganization processes, whose dynamics is encoded in ADMs. Using the definition of the first-tier excited-state ADM in Eq. (45) and specializing to the single-chromophore case and impulsive excitation, we obtain

\[
\sigma_{ee, m_o}(t) = -2 \frac{\varepsilon_e^2}{\hbar^2} \left( 1 - e^{-\mu_{m_o} t/\hbar} \right) P_e |e\rangle\langle e|.
\]

(49)

In essence, the only nontrivial contribution comes from the anticommutator with \( |e\rangle\langle e| \), which produces a factor of 2. A similar analysis can be conducted for \( d \)-thTier \( (d \geq 1) \) excited-state ADM with the final result

\[
\sigma_{ee, m_{o_1} \ldots m_{o_d}}(t) = (-2)^d \prod_{p=1}^d \left( \frac{\varepsilon_{m_p}^2}{\hbar^2} \frac{1 - e^{-\mu_{m_p} t}}{\mu_{m_p}} \right) P_e |e\rangle\langle e|.
\]

(50)
Therefore, within the pure-dephasing spin–boson model, we can analytically compute the nonequilibrium environmental dynamics initiated by a delta-like photoexcitation. The result embodied in Eq. (50) becomes particularly interesting in the archetypal case of Drude–Lorentz spectral density

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

(51)

when only the coefficient \(c_0\) connected to the Drude pole \(\mu_0 = \gamma\) has an imaginary part [see also Eq. (15)]

\[
c_0 = \lambda \cdot \hbar \gamma \left[ \cot \left( \frac{\beta \hbar \gamma}{2} \right) - 1 \right].
\]  

(52)

In this case, the only excited-state ADMs which exhibit a nontrivial temporal evolution are the ones featuring an exclusive excitation of the Drude pole. After performing suitable rescalings, which ensure that ADMs are dimensionless and indeed decay to zero in high enough hierarchical orders \(^{61}\), we finally obtain for \(d \geq 0\)

\[
\langle \sigma | \rho_{ee,0_{m_1} \ldots m_d}^{\text{resc}}(t) | \sigma \rangle / P_e = \delta_{m_1,0} \ldots \delta_{m_d,0} \times
\]

\[
x \cdot \frac{2t}{\sqrt{d!}} \left( \frac{\lambda}{\hbar \gamma} \right)^{d/2} \left[ 1 + \cot^2 \left( \frac{\beta \hbar \gamma}{2} \right) \right]^{-d/4} \left( 1 - e^{-\gamma t} \right)^d.
\]  

(53)

In Fig. 3, we present the time evolution of the RDM and first four nontrivial ADMs that is predicted by Eq. (53). The numerical computations of the dynamics of impulsively photoexcited spin–boson model performed in Ref. 48 (see Fig. 1 and the corresponding discussion) employed the high-temperature approximation, in which the expansion of the bath correlation function [Eq. (14)] contains only the Drude contribution (term with \(m = 0\)). Interestingly, our analytical result [Eq. (53)] demonstrates that, in that case, the high-temperature approximation actually gives an exact solution.

Let us also note that the procedure outlined can be repeated to obtain optical-coherence ADMs. However, judging by Eq. (42), there will be no restrictions on states that can be excited. This is not at variance with constraints present in Eq. (53) because, in the impulsive limit, optical coherences are not sources for purely excited-state dynamics.

### B. Redfield Theory with Photoexcitation

Let us now demonstrate how, in the limit of weak excitation–environment interaction, our results for \(\rho_{\text{ee}}^{(I)}(t)\) and \(\rho_{\text{eg}}^{(I)}(t)\) reduce to the results of Ref. 29 and 35, where the photoexcitation is treated up to the second order in the optical field, while the environment-induced relaxation processes are described within the Redfield theory. The strategy that we use is similar to the one used in Ref. 48 to accomplish a similar goal.

Taking time derivative of Eq. (34), we obtain

\[
\partial_t \rho_{ee}^{(I)}(t) = -\frac{i}{\hbar} \rho_{eg}^{(I)}(t) \mu_{ge}^{(I)}(t) \cdot \mathbf{E}(t) + \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \partial_t \rho_{\text{ee}}^{(I)}(t, t_2, t_1) A^{(I)}(t_2, t_1) + \text{H.c.}
\]  

(54)
The time derivative of the reduced evolution superoperator reads as

\[
\partial_t \tilde{U}_{\text{red}}^{(1)}(t, \tau_2, \tau_1) = - \sum_j V_j^{(1)}(t)x \times T \left\{ \int_0^{t-\tau_2} ds \left( \frac{C_j^r(s)}{\hbar^2} V_j^{(1)}(t-s) + i \frac{C_j^i(s)}{\hbar^2} V_j^{(1)}(t-s)^0 \right) + \int_{t-\tau_2}^{t-\tau_1} ds \frac{C_j(s)}{\hbar^2} V_j^{(1)}(t-s)^C \right\} \tilde{U}_{\text{red}}^{(1)}(t, \tau_2, \tau_1) \right\} \tag{55}
\]

If we now assume that the characteristic decay time of the bath correlation function \( C_j(t) \) is short compared to the time scales of the dynamics we are interested in, we can formally set \( t-\tau_2 \to +\infty \). Then, the second integral on the right-hand side of Eq. (55) is equal to zero, while in the first integral we can invoke Markovian approximation \( [43] \), which enables us to formally move hyperoperators \( V_j^{(1)}(t-s)^x/\circ \) in front of the \( T \) sign. Transferring back to the Schrödinger picture, we obtain

\[
\partial_t \rho_{ee}(t) = - \frac{i}{\hbar} [H_M, \rho_{ee}(t)] - \frac{i}{\hbar} \rho_{eg}(t) \mu_{ge} \cdot \mathcal{E}(-)(t) + \frac{i}{\hbar} \mathcal{E}(+)(t) \cdot \mu_{eg} \rho_{eg} - \sum_j V_j^x \left[ \Lambda_j \rho_{ee}(t) - \rho_{ee}(t) \Lambda_j^\dagger \right], \tag{56}
\]

where

\[
\Lambda_j = \int_0^{+\infty} ds \frac{C_j(s)}{\hbar^2} e^{-iH_M s/\hbar} V_j e^{iH_M s/\hbar}. \tag{57}
\]

Repeating the same steps on Eq. (56), we obtain the following second-order equation for optical coherences

\[
\partial_t \rho_{eg}(t) = - \frac{i}{\hbar} [H_M, \rho_{eg}(t)] + \frac{i}{\hbar} \mu_{eg} \cdot \mathcal{E}(+)(t) |g\rangle \langle g| - \sum_j V_j \Lambda_j \rho_{eg}(t). \tag{58}
\]

Further manipulations towards the Redfield equation take place in the excitonic basis \( \{|x\rangle\} \), defined by \( H_M| x\rangle = \omega_x | x\rangle \). Having performed them, we conclude that optical coherence \( y_{x}(t) = \langle x| \rho_{eg}(t) |g\rangle \) evolves as

\[
\partial_t y_x(t) = -i \omega_x y_x(t) + \frac{i}{\hbar} \mu_x \cdot \mathcal{E}(+)(t) - \sum_{x'} \left( \sum_{\bar{x}} \Gamma_{x\bar{x}x'} \right) y_{x'}(t), \tag{59}
\]

while exciton populations and intraband coherences \( n_{\bar{x}x}(t) = \langle x| \rho_{ee}(t) |\bar{x}\rangle \) obey

\[
\partial_t n_{\bar{x}x}(t) = -i (\omega_{\bar{x}} - \omega_x) n_{\bar{x}x}(t) - \frac{i}{\hbar} \mu_{\bar{x}} \cdot \mathcal{E}(+)(t) y_x(t) + \frac{i}{\hbar} y_x(t) \mu_x \cdot \mathcal{E}(+)(t) - \sum_{\bar{x}'x'} R_{\bar{x}x\bar{x}'x'} n_{\bar{x}'x'}(t). \tag{60}
\]

In Eq. (59), the damping matrix \( \Gamma_{x\bar{x}x'} \) is defined as

\[
\Gamma_{x\bar{x}x'} = \sum_j \langle x|j\rangle \langle j|x'\rangle \langle \bar{x}|j\rangle \langle j|\bar{x}'\rangle \times
\]

\[
\times \int_0^{+\infty} ds \frac{C_j(s)}{\hbar^2} e^{i(\omega_{\bar{x}} - \omega_x)s}, \tag{61}
\]

while the Redfield tensor \( R_{\bar{x}x\bar{x}'x'} \) appearing in Eq. (60) assumes the standard form

\[
R_{\bar{x}x\bar{x}'x'} = -\Gamma_{x\bar{x}x'} - \Gamma_{x'\bar{x}'x} + \delta_{x\bar{x}} \sum_{x'} \Gamma_{x'\bar{x}'x'} + \delta_{x'\bar{x}'} \sum_x \Gamma_{x\bar{x}x'}. \tag{62}
\]

We have also introduced elements of the dipole-moment operator in the excitonic basis \( \mu_x = \langle x| \mu_{eg} |g\rangle \).

In applications, it is common to neglect the imaginary parts of the Redfield tensor \( [29, 43] \), which give rise to renormalizations of transition frequencies. However, as discussed in Ref. [62], this is not correct, especially when we discuss the Redfield equation without the secular approximation. Moreover, as the following discussion demonstrates, the application of Eqs. (55) and (60) to describe laser-induced dynamics of electronic excitations that are strongly coupled to relatively slow nuclear motions runs into more serious difficulties than those caused by neglecting renormalizations of transition frequencies or applying the secular approximation.

In Figs. (a) (f) we compare the photoinduced electronic dynamics of a dimer treated by our HEOM formalism incorporating the photoexcitation [Eqs. (19) and (20)] and the Redfield formalism incorporating the photoexcitation [Eqs. (59) and (60)]. For the weakest excitation–environment coupling, see Figs. (a) and (b), the results predicted by the two approaches are quite similar, as expected. However, as the excitation–environment coupling is increased, the dynamics predicted by the Redfield theory deviates both qualitatively
tion of the pulse is dimer is areas. The difference between local energy levels of the metabolism incorporating the photoexcitation \([Eqs. (19) and (20), solid curves]\) and the Redfield theory incorporating the photoexcitation \([Eqs. (59) and (60), dash-dotted curves]\), while the envelope of the photoexcitation is represented by shaded areas. The difference between local energy levels of the dimer is \(\varepsilon_1 - \varepsilon_2 = 100 \text{ cm}^{-1}\), and the electronic coupling is \(J_{12} = 100 \text{ cm}^{-1}\). The transition dipole moment of site 2 is assumed to be perpendicular to the polarization vector of the exciting field, whereas the magnitude of the projection of the transition dipole moment of site 1 onto the polarization vector is \(d_{10}\). The spectral density of the excitation–environment interaction is assumed to be the Drude–Lorentz spectral density, see Eq. (51), whose parameters \(\gamma\) and \(\lambda\) are identical on both sites. The bath relaxation time is \(\gamma^{-1} = 100\text{ fs}\), while the temperature is \(T = 300\text{ K}\). The waveform of the excitation is \(\mathcal{E}(t) = \frac{1}{\sqrt{2\pi}} \exp\left(-i\Omega_0 t - t^2/(2\tau_p^2)\right)\), where the duration of the pulse is \(\tau_p = 20\text{ fs}\), while the central frequency \(\Omega_0\) is tuned to the vertical transition frequency of site 1. The reorganization energy assumes the following values: \(\lambda = 2 \text{ cm}^{-1}\) in (a) and (b), \(\lambda = 20 \text{ cm}^{-1}\) in (c) and (d), and \(\lambda = 100 \text{ cm}^{-1}\) is (e) and (f).

(e.g., absence of oscillatory features) and quantitatively from the numerically exact results, see Figs. (c)–(f). The reasons for such deviations are summarized in the following.

Firstly, the relaxation tensor employed in Eqs. (59) and (60) is time-independent, i.e., it cannot accurately capture the very first steps of the nuclear reorganization dynamics initiated by photoexcitation. In the derivation presented above, we managed to get a time-local equation for RDM because we ceased to keep track of the exact instants of the interaction with light by formally setting the difference between the observation instant \(t\) and the last instant of the interaction with light \(\tau\) to infinity. Such an approximation is reasonable whenever the bath correlation time and/or the excitation–environment coupling are small enough. These conditions are typically satisfied in ultrafast semiconductor optics \([30, 31]\), which explains the success of methods relying on equations such as Eqs. (59) and (60) to describe ultrafast semiconductor dynamics. On the other hand, in view of the intermediate regime to which photosynthetic EET belongs \([2, 3, 12]\), transient features of light-triggered nuclear reorganization dynamics become crucial to properly characterize electronic dynamics in photosynthetic aggregates. In other words, one has to keep track of the exact instants \(\tau_1\) and \(\tau_2\) of the interaction with light, which our formalism manifestly does. One may hope to partially cure the deficiencies of the dynamics predicted by Eqs. (59) and (60) by replacing the time-independent Redfield tensor by its time-dependent counterpart, see, e.g., Ref. [27]. However, as argued in Supporting Information to Ref. [28], such a replacement in a time-local equation for RDM would have to rely on the rather arbitrary instant \(t_0\) in which we prescribe the initial condition \([Eq. (11)]\), which would give a reasonable description only in the limit of impulsive excitation at \(t_0\). For pulses of finite duration, the correct description of ultrafast dynamics has to be on the time-nonlocal level.

Secondly, the neglect of the second integral on the right-hand side of Eq. (55) actually means that Eqs. (59) and (60) neglect the nonequilibrium dynamics of the bath in the period between the two interactions with light. Again, our formalism manifestly includes such dynamics through the HEOM for optical coherences. On the other hand, change in the bath state in the period between the two interactions with the light can be partially taken into account, even on the time-local level, through the so-called photoinduced correlation term that was identified in Ref. [25] (and also, in a more specialized setting, in Ref. [27]). In the language of the standard density matrix theory, the photoinduced correlation term arises from the combined action of the environmental assistance and the interaction with the exciting field. For more details, see Sec. III of Ref. [50] (Supplemental Material to this manuscript).

C. Nonequilibrium Generalization of Förster Theory

As pointed out in Ref. [48], the Förster limit \([63]\) cannot be directly obtained from the analytical results presented there, simply because the initial environmental density matrix \(\rho_B^0\) is assumed to describe the equilibrium of environmental modes when there are no electronic excitations in the system. However, in the following, we demonstrate...
how, under appropriate approximations, the results of Ref. [38], i.e., our results in the limit of ultrashort excitation, lead to the nonequilibrium generalization of the Förster theory proposed in Ref. [64] and [65].

Let us limit our discussion to an aggregate containing two chromophores, one acting as the excitation donor (D), and the other as the excitation acceptor (A). The Hamiltonian $H_M$ [Eq. (65)] can then be written as

$$H_M = \varepsilon_D |D\rangle\langle D| + \varepsilon_A |A\rangle\langle A| + J_{DA} (|A\rangle\langle D| + |D\rangle\langle A|)$$

$$= H_D + H_A + H_{DA}. \quad (63)$$

Let an impulsive excitation selectively excite $D$ at $t = 0$. Disregarding the dynamics of thus induced optical coherences, the reduced excited-state dynamics for $t > 0$ is described by

$$\rho^{(I)}_{ee}(t) = T \exp \left[ \tilde{W}^{(I)}_{p}(t, 0) \right] |D\rangle\langle D|,$$  \quad (64)

where we have dropped out the normalization constant similar to $P^e$ in Eq. (16).

In the Förster limit, $H_{DA}$ defined in Eq. (65) is assumed to be small, so that $V_j^{(I)}(s) \approx V_j$, similarly to the single-chromophore case studied in Sec. [3A]. We are interested in the rate at which the population of $A$,

$$P_A(t) = \langle A|\tilde{U}_{DA}(t, 0)\rho^{(I)}_{ee}(t)\tilde{U}^*_D(t, 0)|A\rangle,$$  \quad (65)

changes. In the last equation, a tilde over operator denotes the interaction picture with respect to $H_D + H_A$, and

$$\tilde{U}_{DA}(t, 0) = T \exp \left[ -\frac{i}{\hbar} \int_0^t ds \tilde{H}_{DA}(s) \right]. \quad (66)$$

Equation (66) takes into account all possible ways in which the population transfer from $D$ to $A$ may occur, including the ones arising due to the combined action of environmental assistance and $H_{DA}$. However, in the Förster theory, the population transfer is induced by two actions of $H_{DA}$ on opposite sides of $|D\rangle\langle D|$, while environmental DOFs are mere spectators in that process. Nevertheless, they do adapt to the change of electronic state induced by the transfer, but they alone cannot induce it if we assume (as is usual) that no environmental mode couples to both $D$ and $A$ [64]. The situation is somehow similar to the photoexcitation process, where the excited-state sector $ee$ is reached from the ground-state sector $gg$ by applying two $H_{M-R}$ from the opposite sides of $|g\rangle\langle g|$. The phonons just adapt to the new electronic configuration, but they alone cannot bring about to the ground-to-excited state transition. Having all these things considered, it seems reasonable to attempt to replace all time-dependent operators $V_j^{(I)}(t)$ in Eq. (64) by time-independent operators $V_j$ and to transform Eq. (66) by expanding $\tilde{U}_{DA}(t, 0)$ and keeping only contributions in which two $\tilde{H}_{DA}(\tau)$ act from the opposite sides of $\rho^{(I)}_{ee}(t)$. This results in the following expression for the $D \to A$ transfer rate

$$k_{AD}(t) = \frac{2}{\hbar^2} \int_0^t d\tau \text{Re} \left\{ \langle A| \tilde{H}_{DA}(\tau) T \exp \left[ \tilde{W}^{(I)}_{p}(t, 0) \right] |D\rangle\langle D| \tilde{H}_{DA}(\tau) |A\rangle \right\}. \quad (67)$$

Further transformation towards the Förster limit exploit the analogy with the photoexcitation process, where the full hyperoperator notation of Eq. (38) is particularly useful. Equation (38) suggests that Eq. (67) is reduced to the Förster limit by enforcing the global chronological order in the hyperoperator product acting on $|D\rangle\langle D|$, i.e.,

$$k^F_{AD}(t) = \frac{2}{\hbar^2} \int_0^t d\tau \text{Re} \left\{ \langle A| T \tilde{H}^C_{DA}(\tau) \exp \left[ \tilde{W}^{(I)}_{p}(t, 0) \right] C \tilde{H}^C_{DA}(\tau) |D\rangle\langle D| |A\rangle \right\}. \quad (68)$$

We partition the integration domain in $\tilde{W}^{(I)}_{p}(t, 0)$ as follows $[F^{(I)}_{p}(s_2, s_1)]$ denotes the hyperoperator under integral signs in Eq. (38):

$$\tilde{W}^{(I)}_{p}(t, 0) = \int_0^\tau ds_2 \int_0^{s_2} ds_1 \tilde{F}^{(I)}_{p}(s_2, s_1) + \int_\tau^t ds_2 \int_\tau^{s_2} ds_1 \tilde{F}^{(I)}_{p}(s_2, s_1) + \int_\tau^t ds_2 \int_0^\tau ds_1 \tilde{F}^{(I)}_{p}(s_2, s_1). \quad (69)$$

Let us now analyze Eq. (68) order by order in $\tilde{W}^{(I)}_{p}(t, 0)$. The approximation $V_j^{(I)}(s) \approx V_j$ is performed only after the global time-ordering prescription has been applied. Let us focus on the first-order term. The first summation on the right-hand side of Eq. (68) describes the single-phonon assistance before the first interaction $H_{DA}$ takes place at instant $\tau$. Upon making the approximation $V_j^{(I)}(s) \approx V_j$, we conclude that the corresponding contribution is equal to zero (cf. Sec. [3A]). The second summand in Eq. (69) is effective after the first interaction $H_{DA}$, when the electronic state is that of $D/A$ coherence, $|D\rangle\langle A|$. It is then easily checked that [see also Eq. (45)]

$$T \tilde{H}^C_{DA}(\tau) \int_\tau^t ds_2 \int_\tau^{s_2} ds_1 \tilde{F}^{(I)}_{p}(s_2, s_1) C \tilde{H}^C_{DA}(\tau) |D\rangle\langle D| \approx -J_{DA}^2 e^{-i(\varepsilon_D - \varepsilon_A)(t-\tau)} |g_D(t-\tau) + g_A^*(t-\tau)| |A\rangle\langle A|. \quad (70)$$
We may anticipate that, after the resummation, this term produces the well-known factors characteristic of donor emission \((e^{-\delta_D(t-\tau)})\) and acceptor absorption \((e^{-\delta_A(t-\tau)})\). In the third summand in Eq. (69), one superoperator acts before, and the other after, the first interaction \(H_{DA} \). This summand is expected to take into account corrections to the aforementioned donor emission factor due to the fact that donor environment has not yet adapted to the electronic excited state. In greater detail,

\[
T \left[ H_{DA}(t)C \int_0^\tau ds_1 \widetilde{F}_p(s_2, s_1) C H_{DA}(\tau) \right] |D\rangle\langle D| \approx -J_{DA}^2 e^{-i(\varepsilon_D - \varepsilon_A)(t-\tau)} \frac{2i}{h^2} \int_0^\tau ds_2 \int_0^\tau ds_1 C_D^* (s_2 - s_1) |A\rangle\langle A|.
\]

(71)

One can convince themselves that the final result for the excitation transfer rate \(k^E_{AD}(t)\) in this limit reads as

\[
k^E_{AD}(t) = \frac{2J_{DA}^2}{\hbar^2} \int_0^\tau d\tau \text{Re} \left\{ \exp \left( i(\varepsilon_D - \varepsilon_A)(t-\tau) - g_D^*(t-\tau) - g_A(t-\tau) + \frac{2i}{\hbar^2} \int_0^\tau ds_2 \int_0^\tau ds_1 C_D^*(s_2 - s_1) \right) \right\}
\]

(72)

To enable a direct comparison with Eq. (20) or Eq. (24) of Ref. 64, one should perform change of variables \(t - \tau = \tau'\) and calculate all bath correlation functions by definition, starting from the general expression for \(u_j\) [Eq. (5)].

VI. EXCITATION BY WEAK INCOHERENT LIGHT

Here, we study in more detail the excitation by (weak) incoherent light, when the factorized part [Eq. (22)] of the first-order light correlation function [Eq. (21)] identically vanishes. Such a situation arises, for example, when exciting by blackbody radiation at temperature \(T_R\), whose state can be described via

\[
\rho_R = \frac{\exp \left[ -\beta_R \sum_{k\lambda} \hbar \omega_k a_{k\lambda}^\dagger a_{k\lambda} \right]}{\text{Tr}_R \exp \left[ -\beta_R \sum_{k\lambda} \hbar \omega_k a_{k\lambda}^\dagger a_{k\lambda} \right]}.
\]

(73)

where \(\beta_R = (k_B T_R)^{-1}\), \(k\) is photon wavevector, \(\lambda\) enumerates two independent polarization states, while operators \(a_{k\lambda}^\dagger\) and \(a_{k\lambda}\) respectively create and annihilate one photon in mode \((k\lambda)\). In that case, the stationarity of the radiation state implies that \(G^{(1)}_{ij}(\tau_2, \tau_1)\) does not depend separately on interaction instants \(\tau_2\) and \(\tau_1\), but only on their difference \(\tau_2 - \tau_1\).

For three-dimensional photon gas at temperature \(T_R\) [Eq. (73)], the evaluation of \(G^{(1)}_{ij}(\tau_2 - \tau_1)\) can be conducted in the standard manner to yield 66

\[
G^{(1)}_{ij}(\tau) = \delta_{ij} \frac{\hbar}{6\pi^2 \varepsilon_0 c^3} \int_0^{+\infty} d\omega \frac{\omega^3}{e^{\beta_R \hbar \omega} - 1} e^{i\omega \tau}.
\]

(74)

Properties of this correlation function, i.e., the temporal coherence of the blackbody radiation, were studied in detail in Refs. 67 and 68. It was concluded that the coherence lifetime, i.e., the characteristic time scale on which \(G^{(1)}_{ij}(\tau)\) exhibits decay as \(\tau\) is increased, is \(\tau_{\text{coh}} \sim \hbar/(k_B T_R)\). For blackbody radiation at \(T_R = 6000\) K, \(\tau_{\text{coh}} \sim 1\) fs. Remembering that the electronic couplings, reorganization energies, and (static) disorder in photosynthetic molecular aggregates typically assume values \(\sim 10-100\) cm\(^{-1}\)2, we conclude that \(\tau_{\text{coh}}\) is at least an order of magnitude shorter than other relevant time scales in the problem. We may then argue that we can disregard the nonequilibrium environmental dynamics taking place between the two interactions with the radiation, which was crucial to correctly describe excitonic dynamics induced by a pulsed photoexcitation, see the discussion accompanying Figs. 4(a)–4(f). In other words, we may assume that both interactions with the radiation occur essentially at the same time. Formally, this limit is achieved by performing the so-called Weisskopf–Wigner approximation 69. This should be done in the excitonic basis \(|\{x\}\rangle\) 70. Since the quantum-optical limit is performed in the standard manner, a detailed presentation of the derivation of \(\rho^{(l)}_{el}(t)\), and subsequently the HEOM, is deferred for Sec. IV of Ref. 50 (Supplemental Material to this manuscript). Here, we only cite the final equation of motion for \(\sigma_{ee,nn}(t)\)

\[
\partial_t \sigma_{ee,nn}(t) = -\frac{i}{\hbar} \left[ H_M, \sigma_{ee,nn}(t) \right] - \left( \sum_{m} \sum_{n} n_{j,m} \mu_{j,m} \sigma_{ee,nn}(t) \right) + \delta_{n,0} \sum_{x} \frac{\mu_x \cdot \mu_x}{|\mu_x|^2} \frac{1}{2} \Gamma_x n_{BE}(\omega_x, T_R) |x\rangle \langle x| + \delta_{n,0} \sum_{x} \frac{\mu_x \cdot \mu_x}{|\mu_x|^2} \frac{1}{2} \Gamma_x n_{BE}(\omega_x, T_R) |x\rangle \langle x| + \sum_{j} \sum_{m} \left[ V_j, \sigma_{ee,n^+_m}(t) \right] + \sum_{j} \sum_{m} n_{j,m} \left( \frac{c_{j,m}}{\hbar^2} V_j \sigma_{ee,n^-_m}(t) - \frac{c_{j,m}}{\hbar^2} \sigma_{ee,n^-_m}(t) V_j \right).
\]

(75)

where

\[
n_{BE}(\omega_x, T_R) = \left( e^{\beta_R \hbar \omega_x} - 1 \right)^{-1}, \quad \text{while } \Gamma_x = \text{the so-called Weisskopf–Wigner spontaneous}
\]


emission rates from excitonic state $|x\rangle$.

$$
\Gamma_x = \frac{1}{4\pi\varepsilon_0} \frac{4\mu_x^3}{3\hbar c^3}.
$$

In Eq. (77), the generation of excited-state populations and intraband coherences from the ground state is described by the source terms containing excitonic dipole moments, spontaneous emission rates, and Bose–Einstein factors. The rate at which the population of excitonic state $|x\rangle$ is generated from the ground state assumes the familiar form

$$
(\partial_t n_{xx}(t))_{\text{source}} = \Gamma_x n_{\text{BE}}(\omega_x, T_R),
$$

where the spontaneous emission rate $\Gamma_x$ is multiplied by the Bose–Einstein factor, which is characteristic for the absorption of one photon of energy $\hbar\omega_x$. The rate at which the intraband coherence between excitonic states $|\tilde{x}\rangle$ and $|x\rangle$ ($\tilde{x} \neq x$) is generated from the ground state contains factors $\mu_{\tilde{x}} \cdot \mu_{x}^\ast$, describing the alignment of the corresponding transition dipole moments

$$
(\partial_t n_{xx}(t))_{\text{source}} = \frac{\mu_{\tilde{x}} \cdot \mu_{x}^\ast}{|\mu_x|^2} \frac{1}{2} \Gamma_x n_{\text{BE}}(\omega_x, T_R).
$$

Interestingly, these source terms are present exclusively in the equation for the RDM, as indicated by the presence of the Kronecker delta $\delta_{n,0}$. At first sight, this is very different from the description of the light–matter interaction on the quantum-optical level in Ref. [37], which is inspired by the combined Born–Markov–HEOM approach developed in Ref. [71]. There, each level of the hierarchy contains source terms similar to the ones we encounter in Eq. (75) on the level of the RDM. Moreover, the quantum-optical source terms in Ref. [37] also feature the radiative recombination terms, which deplete excited-state populations and increase the ground-state population. The reason for such differences lies in the fact that our treatment of the photoexcitation process starts from the unexcited system and is consistently up to the second order in the exciting field. Within our approximations, the ground-state population is always close to 1, and the excited-state populations are at least quadratic in the weak exciting field and are much smaller than 1, cf. Eqs. (18a) and (18b). We have already used similar arguments to transform Eq. (16) to Eqs. (19) and (20). Here, on the quantum-optical level, the generation rate of excited-state populations, Eq. (75), implicitly contains our assumption that, at all times, the ground-state population differs from 1 by a quantity that is at least quadratic in the exciting field. Similar terms for higher-tier ADOs are absent in our treatment simply because their ground-state expectation values are approximately 0 at all times. In a similar vein, our treatment cannot capture radiative recombination from excited states because that process is at least of the fourth order in the field.

We continue by discussing the most general case, in which we do not rely on approximations of the quantum-optical type. The HEOM, as is formulated here, leans on the exponential decomposition of the environmental correlation function $C_{ij}(t)$, see Eq. (14). Therefore, it may be expected that, if we can expand $G_{ij}^{(1)}(\tau_2 - \tau_1)$ as a weighted sum of exponentially decaying factors, we can proceed to formulate HEOM in the usual manner. Here, we will not dwell on how such an expansion can be done in the case of the first-order radiation correlation function in Eq. (74). We rather concentrate on thermal light whose propagation direction and polarization are well defined. It is known that quantum and classical theory predict the same form of the first-order light correlation function for such light.

$$
G^{(1)}(\tau) = I_0 \exp(i\omega_c\tau - \tau/\tau_c).
$$

Here, $I_0$ is the intensity, $\omega_c$ is the central frequency, while $\tau_c$ is the coherence time of the radiation. In view of the well defined polarization, we omit subscripts $i,j$ labeling Cartesian coordinates of the electric field. This form of the first-order radiation correlation function has been used to gain insight into the dynamics of open [20] and closed [23] quantum systems weakly driven by light. Here, motivated by the aforementioned exponential decomposition, we show how the following light correlation function

$$
G^{(1)}(\tau) = \sum_i I_{0,i} \exp(i\omega_{c,i}\tau - \tau/\tau_{c,i})
$$

can be used to recast Eq. (34) in form of HEOM.

Even though the reduction of the $eg$ sector [Eq. (20)] of the total DM gives zero, the general scheme of the hierarchy is still analogous to that we outlined in the case of classical excitation, see Fig. 2. One can introduce the following objects that act in the $eg$ sector and are thus analogous to optical coherences, cf. Eq. (19).

$$
\rho_{eg,l}^{(1)}(t) = \int_0^t dt' U_{\text{rec}}^{(l)}(t, t') \frac{1}{\hbar} \mu_{eg}^{(l)}(\tau) |g\rangle \langle g| \times I_{0,l} \exp(i\omega_{c,l}(t - \tau) - (t - \tau)/\tau_{c,l}),
$$

where the dipole-moment operator $\mu_{eg}$ is the projection of $\mu_{eg}$ on the polarization direction. These optical coherence-like objects are counted by index $l$ appearing in Eq. (81). In other words, each term in the exponential decomposition of the first-order radiation correlation function adds a new layer to the HEOM for optical co-
Nevertheless, the HEOM for singly excited-state populations and intraband coherences does not feature any additional layers stemming from the decomposition in Eq. (\ref{eq:decomposition}) and it reads as

$$\partial_t \sigma_{eg,l,n}(t) = \frac{i}{\hbar} [H_M, \sigma_{eg,l,n}(t)]$$

$$+ \left( \sum_j \sum_m \mu_{j,m} n_j, m \right) \sigma_{ee,n}(t)$$

$$+ \frac{i}{\hbar} \mu_{eg} \left( \sum_j \sigma_{eg,l,n}^j(t) \right)$$

$$+ i \sum_j \sum_m V_j \sigma_{eg,l,n}^j(t)$$

$$+ i \sum_j \sum_m n_j, m \left( \frac{c_{j,m}}{\hbar} V_j \sigma_{ee,n} \right)_m(t).$$

(\ref{eq:decomposition})

(\ref{eq:realization})

(\ref{eq:observable})

(\ref{eq:master})

VII. CONCLUSION

We have conducted a detailed theoretical investigation of the dynamics of electronic excitations in molecular aggregates induced by weak radiation of arbitrary properties. Starting from initially unexcited aggregate, our approach combines a perturbative treatment of the coupling to radiation with an exact treatment of the excitation–environment coupling in a manner that is manifestly compatible with the spectroscopic view of the photoexcitation. We express the reduced excited-state dynamics entirely in terms of the first-order radiation correlation function and the reduced evolution superoperator, for which we provide an exact expression within the Frenkel exciton model. The changes that the state of electronic excitations undergoes due to the photoexcitation and the interaction with the environment can be conveniently represented diagrammatically, in terms of elementary processes assisted by single quanta of environmental excitations. The fact that our general expression for the excited-state dynamics explicitly keeps track of the instants at which the two interactions with light occur means that the corresponding differential equation is time-nonlocal. Within the exponential decomposition scheme, we outline how this temporal nonlocality can be circumvented by setting up a suitable HEOM scheme that explicitly takes into account the photoexcitation step. Such developments, however, turn out to heavily depend on radiation properties.

In the case of excitation by transform-limited pulses, when the radiation correlation function factorizes into product of (classical) electric fields at two interaction instants, we relate HEOM arising from our results to the HEOM obtained by considering the (semiclassical) light–matter coupling as a part of the aggregate Hamiltonian. The insights from nonlinear spectroscopy and semiconductor optics analyzed using the DCT scheme turn out to be crucial in establishing that relationship. Namely, the order in which the light–matter coupling is taken into account determines the subspace of the excitation Fock space on which the photoinduced dynamics should be formulated, and vice versa. We demonstrate that the second-order response to light should be formulated on the subspace containing at most one excitation.

We analyze in detail the dynamics triggered by an impulsive excitation of a single chromophore, where we
provide analytical results for environmental reorganization dynamics, which is encoded in ADMs. We further identify the approximations under which our general result reduces to the widely employed Redfield theory with photoexcitation and nonequilibrium Förster theory. Our comparison between the dynamics predicted by HEOM and Redfield theory with photoexcitation further corroborates the advantages of our approach, which exactly describes light-induced environmental reorganization processes and fully takes into account the nonequilibrium evolution of the bath between the two interactions with light.

In the case of excitation by thermal light, we compare our approach to the widely used hybrid Born–Markov–HEOM approach, which treats the light–matter coupling within quantum-optical approximations. Since we employ the exponential decomposition scheme, the formulation of HEOM relies on an exponential decomposition of the radiation correlation function. We obtain that the HEOM thus obtained is not significantly more numerically expensive than the HEOM as it is usually formulated. This is because additional layers stemming from the decomposition of radiation correlation function exist only in its optical-coherence-like part, which may be solved completely independently from its excited-state part. This paves the way towards viable computations of the dynamics triggered by natural incoherent light that respects both specific properties of the radiation and the need for a nonperturbative treatment of excitation–environment coupling.

We believe that, despite its unfavorable numerical cost, the approach outlined here can be useful in further investigations of light–induced dynamics in both photosynthetic light-harvesting aggregates and OPVs. In particular, in both types of systems the relation of the insights gained in ultrafast spectroscopies to the actual operation under natural Sunlight illumination has provoked long-standing debates. Therefore, our method stands a chance of bridging these two standpoints and establishing a new viewpoint on energy conversion in these systems, the tasks that are under way in our research groups.

VIII. ACKNOWLEDGMENTS

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