Supplementary Material for: Exact description of excitonic dynamics in molecular aggregates weakly driven by light

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SI. SECOND-ORDER RESPONSE WITHIN SEMICLASSICAL TREATMENT OF LIGHT–MATTER INTERACTION

In this section, we explain in greater detail why, when we study the second-order response, we can safely limit ourselves to the subspace containing at most one excitation.

The full density matrix $W(t)$ describing the combined system of aggregate excitations and environment can be expanded in powers n of the exciting field

$$W(t) = \sum_{n=0}^{+\infty} W^{(n)}(t), \text{ where } W^{(n)}(t) \propto \mathcal{E}^n. \tag{S1}$$

According to the expansion theorem of Ref. 1, the nth order contribution $W^{(n)}(t)$ may be expanded in terms of states containing a definite number of excitations as follows

$$W^{(n)}(t) = \sum_{n'=0}^{n} \sum_{\kappa'\kappa} |n', \kappa', t\rangle\langle n-n', \kappa, t| \, \rho_B(n, n', \kappa, \kappa', t). \tag{S2}$$

Here, $|n', \kappa', t\rangle$ is a number state containing n' excitations characterized by quantum numbers that are collectively denoted as κ', while its explicit time dependence stems from the time dependence of the exciting field. In that sense, state $|n', \kappa', t\rangle$ is not normalized, but rather scales as $\mathcal{E}^{n'}$. The expansion coefficients $\rho_B(n, n', \kappa, \kappa', t)$ are purely environmental operators.

Using the expansion theorem, it can be shown that the second-order response is fully formulated in terms of the following generating functions[2]

$$Y_j^{\alpha\beta} = \left\langle B_j \hat{F}^{\alpha\beta} \right\rangle, \tag{S3}$$

$$N_{ij}^{\alpha\beta} = \left\langle B_i^\dagger B_j \hat{F}^{\alpha\beta} \right\rangle, \tag{S4}$$

where

$$\hat{F}^{\alpha\beta} = \exp\left(\sum_{j\xi} \alpha_{j\xi} b_{j\xi}^\dagger\right) \exp\left(\sum_{j\xi} \beta_{j\xi} b_{j\xi}\right). \tag{S5}$$

$Y_j^{\alpha\beta}$ is the generating function for (environment-assisted) optical coherences, while $N_{ij}^{\alpha\beta}$ is the generating function for (environment-assisted) singly excited-state populations and intraband coherences. A more elaborate analysis shows that (environment-assisted) biexcitonic amplitudes, $\left\langle B_i B_j \hat{F}^{\alpha\beta} \right\rangle$, which also scale as $\mathcal{O}(\mathcal{E}^2)$, do not contribute to the second-order response, so that they are omitted from further discussions.

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Let us now recall that the excitation annihilation operator B_j may be expanded in terms of number states so that it manifestly connects subspaces accommodating different numbers of excitons[3]

$$B_j = |0\rangle\langle 1,j| + \sum_{\substack{k \\ k\neq j}} |1,k\rangle\langle 2,kj| + \dots \tag{S6}$$

Then,

$$\begin{aligned} Y_j^{\alpha\beta} &= \sum_{n=0}^{+\infty}\sum_{n'=0}^{n}\sum_{\kappa'\kappa} \mathrm{Tr}_M \left\{B_j|n',\kappa',t\rangle\langle n-n',\kappa,t|\right\} \ \mathrm{Tr}_B \left\{\hat{F}^{\alpha\beta}\rho_B(n,n',\kappa,\kappa',t)\right\} \\ &= \sum_{n=0}^{+\infty}\sum_{n'=0}^{n}\sum_{\kappa'\kappa} \langle 1,j|n',\kappa',t\rangle\langle n-n',\kappa,t|0\rangle \ \mathrm{Tr}_B \left\{\hat{F}^{\alpha\beta}\rho_B(n,n',\kappa,\kappa',t)\right\} + \\ &+ \sum_{n=0}^{+\infty}\sum_{n'=0}^{n}\sum_{\kappa'\kappa}\sum_{\substack{k \\ k\neq j}} \langle 2,kj|n',\kappa',t\rangle\langle n-n',\kappa,t|1,k\rangle \ \mathrm{Tr}_B \left\{\hat{F}^{\alpha\beta}\rho_B(n,n',\kappa,\kappa',t)\right\} + \dots \end{aligned} \tag{S7}$$

We see that the summand containing $\langle 1,j|n',\kappa',t\rangle\langle n-n',\kappa,t|0\rangle$ is nonzero iff $n = n' = 1$, i.e., in the first order in the exciting field. The summand containing $\langle 2,kj|n',\kappa',t\rangle\langle n-n',\kappa,t|1,k\rangle$ is nonzero iff $n' = 2$ and $n = 3$, i.e., in the third order in the optical field. Therefore, the expansion of the excitation annihilation operator in number states actually reflects the contributions to $Y_j^{\alpha\beta}$ that are linear, cubic, etc. in the exciting field, as predicted by the central theorem of the DCT scheme.[2] The fact that the environment has no impact on scaling relations is apparent in our discussion. Up to the second order in the exciting field, contributions to B_j that involve a state containing more than one particle do not contribute to the response.

In a similar vein,

$$B_i^\dagger B_j = |1,i\rangle\langle 1,j| + \sum_{\substack{k \\ k\neq i, k\neq j}} |2,ik\rangle\langle 2,jk| + \dots \tag{S8}$$

Combining Eqs. (S2), (S4), and (S8), we conclude that all contributions to $B_i^\dagger B_j$ involving states that accommodate more than a single excitation are at least of the fourth order in the exciting field, and, therefore, do not contribute to the second-order response.

If we are to study the second-order response, we can limit our description to subspaces that contain up to one excitation. On the other hand, as described in the main text, once we formulate the model Hamiltonian in the subspace containing at most one excitation, we can consistently formulate the dynamics only up to the second order in the exciting field.

SII. DERIVATION OF THE EXACT EVOLUTION SUPEROPERATOR

Here, we present the derivation of the exact evolution superoperator for a weakly driven excitonic aggregate.

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

$$\partial_t W^{(I)}(t) = -\frac{\mathrm{i}}{\hbar}\left[H_{M-B}^{(I)}(t) + H_{M-R}^{(I)}(t), W^{(I)}(t)\right], \tag{S9}$$

with the factorized initial condition $W^{(I)}(t_0) \equiv W(t_0)$ given in the main text. Here, we define the interaction picture with respect to the non-interacting Hamiltonian

$$H_0 = H_M + H_B + H_R, \tag{S10}$$

so that for any operator O in the Schrödinger picture, the corresponding operator in the interaction picture with respect to H_0 reads as

$$O^{(I)}(t) = U_0^\dagger(t,t_0) O U_0(t,t_0), \tag{S11a}$$

$$U_0(t,t_0) = \exp\left[-\frac{\mathrm{i}}{\hbar} H_0 (t-t_0)\right]. \tag{S11b}$$

The formal solution to Eq. (S9) is

$$W^{(I)}(t) = \sum_{n=0}^{+\infty} \left(-\frac{\mathrm{i}}{\hbar}\right)^n \int_{t_0}^{t} \mathrm{d}\tau_n \cdots \int_{t_0}^{\tau_2} \mathrm{d}\tau_1 \left[H_{M-B}^{(I)}(\tau_n) + H_{M-R}^{(I)}(\tau_n), \ldots, \left[H_{M-B}^{(I)}(\tau_1) + H_{M-R}^{(I)}(\tau_1), W(t_0)\right] \ldots\right]. \tag{S12}$$

Let us now focus on the case of weak interaction with the radiation by keeping in Eq. (S12) only contributions that contain no more than two interaction Hamiltonians H_{M-R}. At the same time, as discussed in Sec. SI, this means that we can safely reduce our description to the subspace containing at most one excitation and consequently make the replacements $B_j \to |g\rangle\langle j|, B_j^\dagger \to |j\rangle\langle g|$ in the model Hamiltonian. The specific form of the initial condition, 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, ge, 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

$$W_{eg}^{(I)}(t) = -\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}\tau\, U_{M-B}^{(I)}(t,\tau) H_{M-R}^{(I)}(\tau) W(t_0), \tag{S13}$$

for the gg sector

$$\begin{aligned} W_{gg}^{(I)}(t) = W(t_0) &- \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}\tau\, H_{M-R}^{(I)}(\tau) W_{eg}^{(I)}(\tau) \\ &+ \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}\tau\, W_{eg}^{(I)\dagger}(\tau) H_{M-R}^{(I)}(\tau), \end{aligned} \tag{S14}$$

and for the ee sector

$$\begin{aligned} W_{ee}^{(I)}(t) = &\int_{t_0}^{t} \mathrm{d}\tau_2 \int_{t_0}^{\tau_2} \mathrm{d}\tau_1\, U_{M-B}^{(I)}(t,\tau_2) U_{M-B}^{(I)}(\tau_2,\tau_1) \left(\frac{1}{\hbar^2} H_{M-R}^{(I)}(\tau_1) W(t_0) H_{M-R}^{(I)}(\tau_2)\right) U_{M-B}^{(I)\dagger}(t,\tau_2) \\ + &\int_{t_0}^{t} \mathrm{d}\tau_2 \int_{t_0}^{\tau_2} \mathrm{d}\tau_1\, U_{M-B}^{(I)}(t,\tau_2) \left(\frac{1}{\hbar^2} H_{M-R}^{(I)}(\tau_2) W(t_0) H_{M-R}^{(I)}(\tau_1)\right) U_{M-B}^{(I)\dagger}(\tau_2,\tau_1) U_{M-B}^{(I)\dagger}(t,\tau_2). \end{aligned} \tag{S15}$$

In Eqs. (S13) and (S15),

$$U_{M-B}^{(I)}(s_2,s_1) = T\exp\left[-\frac{\mathrm{i}}{\hbar}\int_{s_1}^{s_2} \mathrm{d}s\, H_{M-B}^{(I)}(s)\right], \tag{S16}$$

where T denotes the chronological time ordering. The result embodied in Eq. (S15) can be interpreted in terms of double-sided Feynman diagrams.[4] The two summands on the right-hand side of Eq. (S15) 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.[5] 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. (S15) and (S14) 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

$$\rho_{ee}^{(I)}(t) = \mathrm{Tr}_B\left\{\mathrm{Tr}_R\left\{W_{ee}^{(I)}(t)\right\}\right\}. \tag{S17}$$

Let us concentrate on reducing the first term on the right-hand side of Eq. (S15). The partial trace over radiation is computed straightforwardly, since radiation operators enter Eq. (S15) only through the two H_{M-R} terms. In more detail,

$$\frac{1}{\hbar^2}\mathrm{Tr}_R\left\{H_{M-R}^{(I)}(\tau_1)W(t_0)H_{M-R}^{(I)}(\tau_2)\right\} = A^{(I)}(\tau_2,\tau_1)\rho_B^g, \tag{S18}$$

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

$$A^{(I)}(\tau_2,\tau_1) = \frac{1}{\hbar^2}\sum_{i,j} G_{ij}^{(1)}(\tau_2,\tau_1)\left\{\boldsymbol{\mu}_{eg}^{(I)}(\tau_1)\right\}_j |g\rangle\langle g|\left\{\boldsymbol{\mu}_{ge}^{(I)}(\tau_2)\right\}_i. \tag{S19}$$

In Eq. (S19), the sums over i and j are performed over Cartesian components of the electric field, whereas $G_{ij}^{(1)}(\tau_2,\tau_1)$ is defined in the main text. 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.[6] 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 τ_1 and τ_2 with the radiation, as well as the observation instant t. Having taken partial trace over radiation, we now expand each phonon propagator [Eq. (S16)] entering Eq. (S15) in powers of H_{M-B}. Since the averaging is performed over the canonical density matrix of the bath, 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 $C_j(t)$ defined in the main text.[7,8]

To simplify further discussion, we concentrate on the following operator

$$w_{ee,1}^{(I)}(t,\tau_2,\tau_1) = U_{M-B}^{(I)}(t,\tau_2)U_{M-B}^{(I)}(\tau_2,\tau_1)A^{(I)}(\tau_2,\tau_1)\rho_B^g U_{M-B}^{(I)\dagger}(t,\tau_2), \tag{S20}$$

whose partial trace over bath has to be computed. The operator $w_{ee,1}^{(I)}(t,\tau_2,\tau_1)$ describes the state of electronic excitations and the environment at time t when we assume that the first interaction with the radiation takes place at τ_1 from the left, while the second interaction occurs at τ_2 from the right. Upon expanding $U_{M-B}^{(I)}$ in powers of $H_{M-B}^{(I)}$, we obtain

$$\begin{aligned} w_{ee,1}^{(I)}(t,\tau_2,\tau_1) = &\sum_{n=0}^{+\infty}\left(-\frac{\mathrm{i}}{\hbar}\right)^n\frac{1}{n!}\sum_{m=0}^{+\infty}\left(-\frac{\mathrm{i}}{\hbar}\right)^m\frac{1}{m!}\int_{\tau_2}^{t}\mathrm{d}q_n\cdots\int_{\tau_2}^{t}\mathrm{d}q_1\int_{\tau_1}^{\tau_2}\mathrm{d}s_m\cdots\int_{\tau_1}^{\tau_2}\mathrm{d}s_1 \\ & T\left[H_{M-B}^{(I)}(q_n)^\times\ldots H_{M-B}^{(I)}(q_1)^\times\right]\ T\left[H_{M-B}^{(I)}(s_m)^C\ldots H_{M-B}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)\rho_B^g, \end{aligned} \tag{S21}$$

where hyperoperators with superscritps $\times$ and C have the same meaning as in the main text. The index n controls the order of expansion of the combination $U_{M-B}^{(I)}(t,\tau_2)\ldots U_{M-B}^{(I)\dagger}(t,\tau_2)$, and the instants at which individual excitation–environment interactions take place are denoted as $q_1,\ldots,q_n$. Similarly, index m controls the order of expansion of $U_{M-B}^{(I)}(\tau_2,\tau_1)$, and the respective instants are $s_1,\ldots,s_m$. We now use the explicit form of the excitation–environment coupling

$$H_{M-B}^{(I)}(s_1) = \sum_{l_1} V_{l_1}^{(I)}(s_1)u_{l_1}^{(I)}(s_1), \tag{S22}$$

where $V_{l_1}^{(I)}(s_1)$ is a purely electronic operator, while $u_{l_1}^{(I)}(s_1)$ is a purely environmental operator. Let us focus in the following on the operator under sums and integrals in Eq. (S21). Since $A^{(I)}(\tau_2,\tau_1)$ is a purely electronic, while ρ_B^g is a purely environmental operator, we can write

$$\begin{aligned}&T\left[H_{M-B}^{(I)}(q_n)^\times\dots H_{M-B}^{(I)}(q_1)^\times\right]\,T\left[H_{M-B}^{(I)}(s_m)^C\dots H_{M-B}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)\rho_B^g=\\&\sum_{j_n\dots j_1}\sum_{l_m\dots l_1}T\left[\left(V_{j_n}^{(I)}(q_n)u_{j_n}^{(I)}(q_n)\right)^\times\dots\left(V_{j_1}^{(I)}(q_1)u_{j_1}^{(I)}(q_1)\right)^\times\right]\times\\&\times\underbrace{T\left[V_{l_m}^{(I)}(s_m)^C\dots V_{l_1}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)}_{\text{purely electronic}}\,\underbrace{T\left[u_{l_m}^{(I)}(s_m)^C\dots u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g}_{\text{purely environmental}},\end{aligned}\tag{S23}$$

where, in each term of the sum, the hyperoperators from the outermost layer act on an operator that is factorized into a purely electronic and purely environmental part. At this point, the following identity is useful

$$(Vu)^\times O_V O_u=\frac{1}{2}\left(V^\times u^\circ+V^\circ u^\times\right)O_V O_u,\tag{S24}$$

where O_V and O_u are arbitrary operators such that V can act on O_V only, while u can act on O_u only. The last identity enables us to rewrite Eq. (S23) as follows

$$\begin{aligned}&T\left[H_{M-B}^{(I)}(q_n)^\times\dots H_{M-B}^{(I)}(q_1)^\times\right]\,T\left[H_{M-B}^{(I)}(s_m)^C\dots H_{M-B}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)\rho_B^g=\\&\frac{1}{2^n}\sum_{j_n\dots j_1}\sum_{l_m\dots l_1}T\left[\left(V_{j_n}^{(I)}(q_n)^\times u_{j_n}^{(I)}(q_n)^\circ+V_{j_n}^{(I)}(q_n)^\circ u_{j_n}^{(I)}(q_n)^\times\right)\dots\left(V_{j_1}^{(I)}(q_1)^\times u_{j_1}^{(I)}(q_1)^\circ+V_{j_1}^{(I)}(q_1)^\circ u_{j_1}^{(I)}(q_1)^\times\right)\right]\times\\&\times\underbrace{T\left[V_{l_m}^{(I)}(s_m)^C\dots V_{l_1}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)}_{\text{purely electronic}}\,\underbrace{T\left[u_{l_m}^{(I)}(s_m)^C\dots u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g}_{\text{purely environmental}}.\end{aligned}\tag{S25}$$

Each term under multiple sums over js and ls has 2^n summands and, in each of them, the hyperoperators from the outermost layer can be written as

$$V_{j_n}^{(I)}(q_n)^{\bar\sigma_n}u_{j_n}^{(I)}(q_n)^{\sigma_n}\dots V_{j_1}^{(I)}(q_1)^{\bar\sigma_1}u_{j_1}^{(I)}(q_1)^{\sigma_1},$$

where $\sigma_i\in\{\times,\circ\}$, $\bar\times=\circ$, and *vice versa*. Moreover, since all instants $q_n,\dots,q_1$ are certainly later than all instants $s_m,\dots,s_1$, we can merge the two time-ordering signs (one ordering qs and the other ordering ss) into a single time-ordering sign. Having all these transformations performed, we are left with

$$\begin{aligned}&T\left[H_{M-B}^{(I)}(q_n)^\times\dots H_{M-B}^{(I)}(q_1)^\times\right]\,T\left[H_{M-B}^{(I)}(s_m)^C\dots H_{M-B}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)\rho_B^g=\\&\frac{1}{2^n}\sum_{j_n\dots j_1}\sum_{l_m\dots l_1}\sum_{\sigma_n\dots\sigma_1}T\left[V_{j_n}^{(I)}(q_n)^{\bar\sigma_n}\dots V_{j_1}^{(I)}(q_1)^{\bar\sigma_1}V_{l_m}^{(I)}(s_m)^C\dots V_{l_1}^{(I)}(s_1)^C\right]A^{(I)}(\tau_2,\tau_1)\times\\&\times T\left[u_{j_n}^{(I)}(q_n)^{\sigma_n}\dots u_{j_1}^{(I)}(q_1)^{\sigma_1}u_{l_m}^{(I)}(s_m)^C\dots u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g.\end{aligned}\tag{S26}$$

We have thus reduced the problem to the computation of the following trace over the environment

$$\mathrm{Tr}_B\left\{T\left[u_{j_n}^{(I)}(q_n)^{\sigma_n}\dots u_{j_1}^{(I)}(q_1)^{\sigma_1}u_{l_m}^{(I)}(s_m)^C\dots u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g\right\}.\tag{S27}$$

It is clear that this trace may give a nontrivial result only when $n+m$ is even, $n+m=2k$, where $k=1,2\dots$. Let us now start from the simplest case $n+m=2$, in which we face the following possibilities:

1. $n=2$ and $m=0$: environmental assistance is characteristic for the electronic subsystem in the excited-state manifold

$$\begin{aligned}\mathrm{Tr}_B\left\{T\left[u_{j_2}^{(I)}(q_2)^{\sigma_2}u_{j_1}^{(I)}(q_1)^{\sigma_1}\right]\rho_B^g\right\}=&\;\theta(q_2-q_1)\delta_{j_2j_1}\cdot 2^2\left(\delta_{\sigma_2,\circ}\delta_{\sigma_1,\circ}C_{j_1}^r(q_2-q_1)+\delta_{\sigma_2,\circ}\delta_{\sigma_1,\times}\mathrm{i}C_{j_1}^i(q_2-q_1)\right)+\\&+\theta(q_1-q_2)\delta_{j_2j_1}\cdot 2^2\left(\delta_{\sigma_2,\circ}\delta_{\sigma_1,\circ}C_{j_1}^r(q_1-q_2)+\delta_{\sigma_2,\times}\delta_{\sigma_1,\circ}\mathrm{i}C_{j_1}^i(q_1-q_2).\right)\end{aligned}\tag{S28}$$

The corresponding contribution to the partial trace over environment of Eq. (S21) then reads as

$$\begin{aligned}\left[\mathrm{Tr}_B w_{ee,1}^{(I)}(t,\tau_2,\tau_1)\right]_{n=2,m=0} &= -\frac{1}{\hbar^2}\sum_j \int_{\tau_2}^{t}\mathrm{d}q_2 \int_{\tau_2}^{q_2}\mathrm{d}q_1 \times \\ &\times V_j^{(I)}(q_2)^{\times}\left(C_j^r(q_2-q_1)V_j^{(I)}(q_1)^{\times} + \mathrm{i}C_j^i(q_2-q_1)V_j^{(I)}(q_1)^{\circ}\right)A^{(I)}(\tau_2,\tau_1) \\ &\equiv \overrightarrow{\mathcal{W}}_p(t,\tau_2)A^{(I)}(\tau_2,\tau_1),\end{aligned} \tag{S29}$$

which is the familiar form that has been obtained when the propagation is considered only within the excited-state manifold.[9]

2. $n=0$ and $m=2$: environmental assistance is characteristic for the electronic subsystem in the state of optical coherence

$$\begin{aligned}\mathrm{Tr}_B\left\{T\left[u_{l_2}^{(I)}(s_2)^C u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g\right\} &= \theta(s_2-s_1)\delta_{l_2l_1}C_{l_1}(s_2-s_1) + \theta(s_1-s_2)\delta_{l_2l_1}C_{l_1}(s_1-s_2) \\ &\equiv \delta_{l_1l_2}C_{l_1}(|s_2-s_1|).\end{aligned} \tag{S30}$$

The corresponding contribution to the partial trace over environment of Eq. (S21) then reads as

$$\begin{aligned}\left[\mathrm{Tr}_B w_{ee,1}^{(I)}(t,\tau_2,\tau_1)\right]_{n=0,m=2} &= -\frac{1}{\hbar^2}\sum_l \int_{\tau_1}^{\tau_2}\mathrm{d}s_2 \int_{\tau_1}^{s_2}\mathrm{d}s_1\, V_l^{(I)}(s_2)^C\, C_l(s_2-s_1)V_l^{(I)}(s_1)^C\, A^{(I)}(\tau_2,\tau_1) \\ &\equiv \overrightarrow{\mathcal{W}}_c(\tau_2,\tau_1)A^{(I)}(\tau_2,\tau_1).\end{aligned} \tag{S31}$$

3. $n=1$ and $m=1$: environmental assistance straddles over periods in which electronic subsystem is in different states: it starts when the electronic subsystem is in the state of optical coherence, and ends when the electronic subsystem is in the excited-state manifold; here, we obtain the elementary contribution to the so-called straddled evolution

$$\mathrm{Tr}_B\left\{T\left[u_{j_1}^{(I)}(q_1)^{\sigma_1}u_{l_1}^{(I)}(s_1)^C\right]\rho_B^g\right\} = \delta_{\sigma_1,\circ}\delta_{j_1,l_1}\cdot 2C_{j_1}(q_1-s_1). \tag{S32}$$

Note that T sign in the last equation can safely be omitted, since we are sure that $q_1 \geq s_1$. The corresponding contribution to the partial trace over environment of Eq. (S21) then reads as

$$\begin{aligned}\left[\mathrm{Tr}_B w_{ee,1}^{(I)}(t,\tau_2,\tau_1)\right]_{n=1,m=1} &= -\frac{1}{\hbar^2}\sum_j \int_{\tau_2}^{t}\mathrm{d}q_1 \int_{\tau_1}^{\tau_2}\mathrm{d}s_1\, V_j^{(I)}(q_1)^{\times}\, C_j(q_1-s_1)V_j^{(I)}(s_1)^C\, A^{(I)}(\tau_2,\tau_1) \\ &\equiv \overrightarrow{\mathcal{W}}_{c-p}(t,\tau_2,\tau_1)A^{(I)}(\tau_2,\tau_1).\end{aligned} \tag{S33}$$

The above analysis conducted in the lowest order of the perturbation expansion gives us basic building blocks from which higher-order contributions are constructed. This is possible by virtue of the Wick's theorem

$$\mathrm{Tr}_B\left\{T\left[u_{j_{2k}}^{(I)}(q_{2k})\dots u_{j_1}^{(I)}(q_1)\right]\rho_B^g\right\} = \sum_{\text{a.p.p.}}\prod_{a,b}\mathrm{Tr}_B\left\{T\left[u_{j_b}^{(I)}(q_b)u_{j_a}^{(I)}(q_a)\right]\rho_B^g\right\}, \tag{S34}$$

which expresses the (equilibrium) expectation value of the product of $2k$ nuclear displacement operators u as a sum over all possible pairings (a.p.p.) of products of k (equilibrium) expectation values of two nuclear displacement operators. A similar identity also holds on the hyperoperator level, which is relevant to our discussion [see Eq. (S27)]. Namely, since all hyperoperators u^π, where $\pi \in \{\times,\circ,C\}$ are linear in nuclear displacement u, we can use Eq. (S34) to establish the following identity

$$\mathrm{Tr}_B\left\{T\left[u_{j_{2k}}^{(I)}(q_{2k})^{\pi_{2k}}\dots u_{j_1}^{(I)}(q_1)^{\pi_1}\right]\rho_B^g\right\} = \sum_{\text{a.p.p.}}\prod_{a,b}\mathrm{Tr}_B\left\{T\left[u_{j_b}^{(I)}(q_b)^{\pi_b}u_{j_a}^{(I)}(q_a)^{\pi_a}\right]\rho_B^g\right\}. \tag{S35}$$

Equation (S35) provides us with a general recipe to compute the partial trace in Eq. (S27) and, eventually, evaluate the contribution to Eq. (S21) in arbitrary perturbation order defined by values of n and m. The form of Eq. (S35) suggests that all the contributions are indeed expressed in terms of the three elementary (lowest-order) contributions that we have evaluated. However, we should still convince ourselves that all these contributions can be resummed into the form of a time-ordered exponential that presented in the main body of the manuscript.

Since this demonstration is rather formal and not particularly insightful, we only make its sketch for $n+m=2k$, $k\geq 1$. There, we have $2k+1$ different possibilities for n and m. In the sketch, we make use of the so-called polynomial expansion, which states that, for mutually commuting entities x_c, x_p, x_{c-p} we have

$$(x_c+x_p+x_{c-p})^k=\sum_{\substack{l_c+l_p+l_{c-p}=k\\ l_c,l_p,l_{c-p}\geq 0}}\frac{k!}{l_c!l_p!l_{c-p}!}\,x_c^{l_c}x_p^{l_p}x_{c-p}^{l_{c-p}}. \tag{S36}$$

The commutativity in our case is ensured by the presence of the global time-ordering sign.

1. $n=2k$, $m=0$
   The application of Wick's theorem [Eq. (S35)] produces $(2k-1)!!$ terms, and it turns out that all of them are the same. In essence, this follows from the fact that all integrals over $q_{2k},\dots,q_1$ are over the same interval $[\tau_2,t]$ and that T sign enables us to permute at will the hyperoperators it affects. All the contributions contain environmental assistance in the form characteristic for the electronic subsystem in the excited-state manifold. Even though the Heaviside functions in Eq. (S28) order the integration variables in pairs, they do not enforce the global order, so that T sign cannot be removed.

   The factor 2^{-2k} (appearing in front of sums by js and ls) is cancelled by the factor $(2^2)^k$ that emerges from k factors of the type given in Eq. (S28). Then, the total prefactor is

   $$\frac{1}{(2k)!}\cdot(2k-1)!!=\frac{1}{k!}\cdot\frac{1}{2^k},$$

   where $(k!)^{-1}$ is indicative of the k-th order in the expansion of an exponential, whereas $(1/2)^k$ compensates for two equivalent time orderings in Eq. (S28). In Fig. 1 we give the corresponding diagrams for $k=2$.

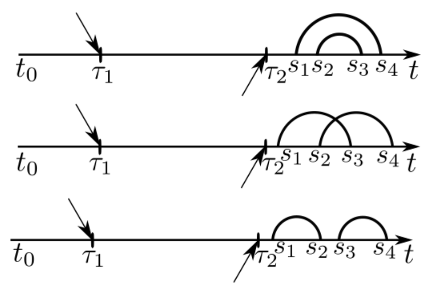

FIG. 1. Diagrams representing different contributions in the fourth-order in H_{M-B} when $n=4$ and $m=0$. Their sum can be understood as the square of the primitive diagram in Fig. 1(b) of the main body of the manuscript. For simplicity, here, we omit information on the state of the electronic subsystem ($|g\rangle$ or $|e\rangle$).

2. $n=2k-1$, $m=1$
   Here, we have one environmental assistance that is mixed (straddled), as in Eq. (S32), and $(k-1)$ assistances that are characteristic for the electronic system in the excited-state manifold, as in Eq. (S28). All the terms produced by the application of Wick's theorem again turn out to be the same. The factor $2^{-(2k-1)}$ (appearing in front of sums by js and ls) is cancelled by the factor $(2^2)^{k-1}\cdot 2$ which stems from $(k-1)$ factors similar to that in Eq. (S28) and one factor similar to that in Eq. (S32). The overall prefactor

   $$\frac{1}{(2k-1)!}\cdot\frac{1}{1!}\cdot(2k-1)!!=\frac{1}{2^{k-1}}\cdot k\cdot\frac{1}{k!}$$

   is then combined with the appropriate term as follows. The factor $(1/2)^{k-1}$ compensates for two equivalent time orderings in each of $(k-1)$ factors analogous to Eq. (S28) (the straddled assistance, by its definition, features a definite time ordering), factor k reflects the fact that there are k equivalent ways of choosing the straddled building block (this is the polynomial coefficient $k!/(l_c!l_p!l_{c-p}!)$ for $l_c=0, l_p=k-1, l_{c-p}=1$), while $(k!)^{-1}$ is again indicative of the k-th order in the expansion of an exponential. In Fig. 2 we give the corresponding diagrams for $k=2$.

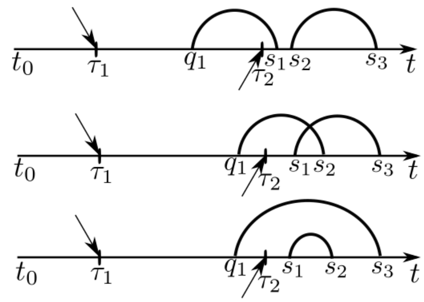

FIG. 2. Diagrams representing different contributions in the fourth-order in H_{M-B} when $n = 3$ and $m = 1$. Their sum can be understood as twice the product of the primitive diagrams in Figs. 1(b) and 1(c) of the main body of the manuscript. For simplicity, here, we omit information on the state of the electronic subsystem ($|g\rangle$ or $|e\rangle$).

3. $n = 2k - 2$, $m = 2$
   Here, we may have

   (a) $(k-1)$ population-like assistances and 1 coherence-like assistance; the number of such terms, which are all mutually identical, is

$$(2(k-1)-1)!! = (2k-3)!!;$$

   (b) $(k-2)$ population-like assistances and 2 straddled assistances; the number of such terms, which are all mutually identical, is

$$(2k-2)(2k-3)(2(k-2)-1)!! = (2k-2)(2k-3)!!.$$

   Of course, the total number of terms produced by the application of Wick's theorem is $(2k-1)!!$. Let us briefly comment on the way how the prefactors combine.

   (a) the prefactor $2^{-(2k-2)}$ (appearing in front of sums over js and ls) is cancelled by the factor $(2^2)^{k-1}$ stemming from $(k-1)$ terms like that in Eq. (S28); the overall prefactor

$$\frac{1}{(2k-2)!} \cdot \frac{1}{2!} \cdot (2k-3)!! = \frac{1}{2^k} \cdot k \cdot \frac{1}{k!}$$

   is combined with the appropriate terms as follows. The factor $(1/2)^k$ compensates for two equivalent time orderings in each of $(k-1)$ factors analogous to Eq. (S28) and the remaining factor analogous to Eq. (S30); factor k is again the polynomial coefficient $k!/(l_c!l_p!l_{c-p}!)$ for $l_c = 1, l_p = k-1, l_{c-p} = 0$;

   (b) the prefactor $2^{-(2k-2)}$ (appearing in front of sums over js and ls) is cancelled by the product $(2^2)^{k-2} \cdot 2^2$ originating from $(k-2)$ factors like that in Eq. (S28) and 2 factors like that in Eq. (S32); in the overall prefactor

$$\frac{1}{(2k-2)!} \cdot \frac{1}{2!} \cdot (2k-2)(2k-3)!! = \frac{1}{2^{k-2}} \binom{k}{2} \frac{1}{k!},$$

   $(1/2)^{k-2}$ compensates for two equivalent time orderings [Eq. (S28)], while $\binom{k}{2}$ is the polynomial coefficient $k!/(l_c!l_p!l_{c-p}!)$ for $l_c = 0, l_p = k-2, l_{c-p} = 2$.

   In Figs. 3(a) and 3(b) we give the corresponding diagrams for $k = 2$.

In a similar manner, one can analyze the remaining terms in order $2k$. The main result of such an analysis is the presence of the factor $1/k!$, as well as the corresponding polynomial factor $k!/(l_c!l_p!l_{c-p}!)$, in each of these terms. Therefore, the resummation produces the time-ordered exponential that is presented in the main text.

(a)

(b)

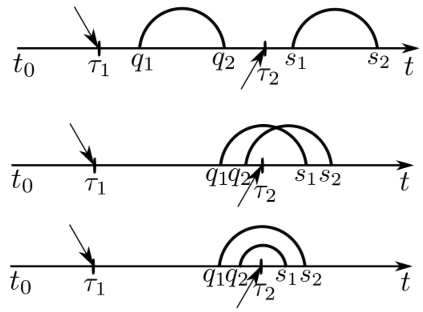

FIG. 3. Diagrams representing different contributions in the fourth-order in H_{M-B} when $n = 2$ and $m = 2$. The diagram in (a) corresponds to the contribution analyzed under point (a) of the discussion and can be understood as twice the product of primitive diagrams in Figs. 1(a) and 1(b) of the main body of the manuscript. The two diagrams in (b) correspond to the contributions analyzed under point (b) of the discussion and can be understood as the square of the primitive diagram in Fig. 1(c) of the main body of the manuscript. For simplicity, here, we omit information on the state of the electronic subsystem ($|g\rangle$ or $|e\rangle$).

Finally, let us present the expression for the reduced evolution superoperator $\overleftarrow{\mathcal{U}}^{(I)}_{\text{red}}(t, \tau_2, \tau_1)$ that acts on the left ($\overline{T}$ denotes antichronological time order)

$$\overleftarrow{\mathcal{U}}^{(I)}_{\text{red}}(t, \tau_2, \tau_1) = \overline{T} \exp\left[\overleftarrow{\mathcal{W}}_c(\tau_2, \tau_1) + \overleftarrow{\mathcal{W}}_p(t, \tau_2) + \overleftarrow{\mathcal{W}}_{c-p}(t, \tau_2, \tau_1)\right], \tag{S37a}$$

$$\overleftarrow{\mathcal{W}}_c(\tau_2, \tau_1) = -\frac{1}{\hbar^2} \sum_j \int_{\tau_1}^{\tau_2} \mathrm{d}s_2 \int_{\tau_1}^{s_2} \mathrm{d}s_1 \, {}^{C}V_j^{(I)}(s_1)\, C_j(s_1 - s_2)\, {}^{C}V_j^{(I)}(s_2), \tag{S37b}$$

$$\overleftarrow{\mathcal{W}}_p(t, \tau_2) = -\frac{1}{\hbar^2} \sum_j \int_{\tau_2}^{t} \mathrm{d}s_2 \int_{\tau_2}^{s_2} \mathrm{d}s_1 \left(C_j^r(s_1 - s_2)\, {}^{\times}V_j^{(I)}(s_1) + \mathrm{i}\, C_j^i(s_1 - s_2)\, {}^{\circ}V_j^{(I)}(s_1) \right) {}^{\times}V_j^{(I)}(s_2), \tag{S37c}$$

$$\overleftarrow{\mathcal{W}}_{c-p}(t, \tau_2, \tau_1) = -\frac{1}{\hbar^2} \sum_j \int_{\tau_2}^{t} \mathrm{d}s_2 \int_{\tau_1}^{\tau_2} \mathrm{d}s_1 \, {}^{C}V_j^{(I)}(s_1)^{\times}\, C_j(s_1 - s_2)\, {}^{\times}V_j^{(I)}(s_2). \tag{S37d}$$

In Eqs. (S37), we define hyperoperators ${}^{\times/\circ/C}V$ acting on the left (which is suggested by the position of the superscript) by the following equalities valid for any operator O

$$O\, {}^{\times}V_j = [O, V_j]\,, \tag{S38a}$$

$$O\, {}^{\circ}V_j = \{O, V_j\}\,, \tag{S38b}$$

$$O\, {}^{C}V_j = OV_j. \tag{S38c}$$

SIII. DERIVATION OF THE REDFIELD EQUATION COMPRISING PHOTOEXCITATION

We start from the central result of our analysis

$$\rho_{ee}^{(I)}(t) = \int_{t_0}^{t} \mathrm{d}\tau_2 \int_{t_0}^{\tau_2} \mathrm{d}\tau_1 \, \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) A^{(I)}(\tau_2,\tau_1) + \mathrm{H.c.} \tag{S39}$$

and specialize to the case of excitation by a weak laser pulse. Taking time derivative of Eq. (S39), we obtain

$$\partial_t \rho_{ee}^{(I)}(t) = -\frac{\mathrm{i}}{\hbar} \rho_{eg}^{(I)}(t) \boldsymbol{\mu}_{ge}^{(I)}(t) \cdot \boldsymbol{\mathcal{E}}^{(-)}(t) + \int_{t_0}^{t} \mathrm{d}\tau_2 \int_{t_0}^{\tau_2} \mathrm{d}\tau_1 \, \partial_t \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) A^{(I)}(\tau_2,\tau_1) + \mathrm{H.c.} \tag{S40}$$

The time derivative of the reduced evolution superoperator reads as

$$\begin{aligned} \partial_t \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) = & -\sum_j V_j^{(I)}(t)^{\times} \\ & \times T \left\{ \left[\int_0^{t-\tau_2} \mathrm{d}s \left(\frac{C_j^r(s)}{\hbar^2} V_j^{(I)}(t-s)^{\times} + \mathrm{i} \frac{C_j^i(s)}{\hbar^2} V_j^{(I)}(t-s)^{\circ} \right) + \int_{t-\tau_2}^{t-\tau_1} \mathrm{d}s \, \frac{C_j(s)}{\hbar^2} V_j^{(I)}(t-s)^{C} \right] \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1) \right\} \end{aligned} \tag{S41}$$

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. (S41) is equal to zero, while in the first integral we can invoke Markovian approximation,[10] which enables us to formally move hyperoperators $V_j^{(I)}(t-s)^{\times/\circ}$ in front of the T sign. Transferring back to the Schrödinger picture, we obtain

$$\partial_t \rho_{ee}(t) = -\frac{\mathrm{i}}{\hbar} \left[H_M, \rho_{ee}(t) \right] - \frac{\mathrm{i}}{\hbar} \rho_{eg}(t) \boldsymbol{\mu}_{ge} \cdot \boldsymbol{\mathcal{E}}^{(-)}(t) + \frac{\mathrm{i}}{\hbar} \boldsymbol{\mathcal{E}}^{(+)}(t) \cdot \boldsymbol{\mu}_{eg} \rho_{eg}^{\dagger}(t) - \sum_j V_j^{\times} \left[\Lambda_j \rho_{ee}(t) - \rho_{ee}(t) \Lambda_j^{\dagger} \right], \tag{S42}$$

where

$$\Lambda_j = \int_0^{+\infty} \mathrm{d}s \, \frac{C_j(s)}{\hbar^2} \, \mathrm{e}^{-\mathrm{i}H_M s/\hbar} V_j \, \mathrm{e}^{\mathrm{i}H_M s/\hbar}. \tag{S43}$$

In an analogous manner, we obtain the following second-order equation for optical coherences

$$\partial_t \rho_{eg}(t) = -\frac{\mathrm{i}}{\hbar} \left[H_M, \rho_{eg}(t) \right] + \frac{\mathrm{i}}{\hbar} \boldsymbol{\mu}_{eg} \cdot \boldsymbol{\mathcal{E}}^{(+)}(t) |g\rangle\langle g| - \sum_j V_j \Lambda_j \rho_{eg}(t). \tag{S44}$$

Further manipulations towards the Redfield equation take place in the excitonic basis $\{|x\rangle\}$. These are quite standard,[10] and result in Eqs. (37) and (38) of the main text.

SIV. EXCITATION BY WEAK INCOHERENT LIGHT: LEVEL OF QUANTUM OPTICAL MASTER EQUATIONS

Here, we demonstrate in more detail how the excitation by weak incoherent light should be handled on the level of quantum optical master equations to produce the HEOM. We start from the general expression for $\rho_{ee}^{(I)}(t)$ [Eq. (S39)] in which we insert the following the radiation correlation function[11]

$$G_{ij}^{(1)}(\tau_2,\tau_1)=\delta_{ij}\,\frac{\hbar}{6\pi^2\varepsilon_0 c^3}\int_0^{+\infty}\mathrm{d}\omega\,\frac{\omega^3}{\mathrm{e}^{\beta_R\hbar\omega}-1}\,\mathrm{e}^{\mathrm{i}\omega(\tau_2-\tau_1)} \tag{S45}$$

to obtain

$$\rho_{ee}^{(I)}(t)=\int_{t_0}^{t}\mathrm{d}\tau_2\int_{t_0}^{\tau_2}\mathrm{d}\tau_1\,\overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_1)\frac{1}{\hbar^2}\left[\boldsymbol{\mu}_{eg}^{(I)}(\tau_1)\cdot\boldsymbol{\mu}_{ge}^{(I)}(\tau_2)\right]\frac{\hbar}{6\pi^2\varepsilon_0 c^3}\int_0^{+\infty}\mathrm{d}\omega\,\omega^3\,n_{\mathrm{BE}}(\omega,T_R)\,\mathrm{e}^{\mathrm{i}\omega(\tau_2-\tau_1)}+ \\ +\,\mathrm{H.c.} \tag{S46}$$

The radiation correlation function in Eq. (S45) is computed for the three-dimensional photon gas at temperature $T_R=(k_B\beta_R)^{-1}$, and $n_{\mathrm{BE}}(\omega_x,T_R)=\left(\mathrm{e}^{\beta_R\hbar\omega_x}-1\right)^{-1}$.

As is usual when the interaction of matter with electromagnetic radiation is treated on the quantum optical level,[12] further developments should be conducted in the eigenbasis of H_M, i.e., in the excitonic basis $\{|x\rangle\}$, whose basis vectors satisfy $H_M|x\rangle=\hbar\omega_x|x\rangle$. Introducing time intervals $t_1=\tau_2-\tau_1$ and $t_2=t-\tau_2$, and transferring to the excitonic basis, we obtain

$$\rho_{ee}^{(I)}(t)=\frac{1}{\hbar^2}\sum_{\bar{x}x}(\boldsymbol{\mu}_{\bar{x}}\cdot\boldsymbol{\mu}_x^*)\int_0^{t-t_0}\mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_{\bar{x}}(t-t_2-t_0)}\,\mathrm{e}^{-\mathrm{i}\omega_x(t-t_2-t_0)}\int_0^{+\infty}\mathrm{d}\omega\,\frac{\hbar}{6\pi^2\varepsilon_0 c^3}\,\omega^3\,n_{\mathrm{BE}}(\omega,T_R)\times \\ \times\int_0^{t-t_0}\mathrm{d}t_1\,\mathrm{e}^{\mathrm{i}(\omega-\omega_{\bar{x}})t_1}\overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,t-t_2,t-t_2-t_1)|\bar{x}\rangle\langle x|+ \\ +\,\mathrm{H.c.} \tag{S47}$$

Further steps are inspired by the Weisskopf–Wigner approximation.[13] Namely, the integral over t_1 contains the phase factor $\mathrm{e}^{\mathrm{i}(\omega-\omega_{\bar{x}})t_1}$ that exhibits oscillatory behaviour unless $\omega\approx\omega_{\bar{x}}$. By employing this approximation in Eq. (S47), the integral over ω reduces to

$$\int_0^{+\infty}\mathrm{d}\omega\,\mathrm{e}^{\mathrm{i}\omega t_1}=\pi\delta(t_1)+\mathrm{i}\mathcal{P}\left(\frac{1}{t_1}\right), \tag{S48}$$

where $\mathcal{P}$ denotes the Cauchy principal value. In the spirit of Weisskopf–Wigner approximation, the part containing the principal-value sign is neglected, and the integration over t_1 is performed to arrive at

$$\rho_{ee}^{(I)}(t)=\sum_{\bar{x}x}(\boldsymbol{\mu}_{\bar{x}}\cdot\boldsymbol{\mu}_x^*)\int_{t_0}^{t}\mathrm{d}\tau_2\,\frac{\omega_{\bar{x}}^3}{6\pi\varepsilon_0\hbar c^3}\,n_{\mathrm{BE}}(\omega,T_R)\overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2)\,\mathrm{e}^{\mathrm{i}\omega_{\bar{x}}(\tau_2-t_0)}|\bar{x}\rangle\langle x|\,\mathrm{e}^{-\mathrm{i}\omega_x(\tau_2-t_0)}+ \\ +\,\mathrm{H.c.} \tag{S49}$$

where we have also restored the interaction instant τ_2 as the integration variable. It is now apparent that the quantum-optical limit is intimately connected to the white-noise model considered in the main text. In both cases, the coherence time of the radiation is assumed to be negligible compared to other relevant time scales in the problem, so that both interactions with the radiation take place at the same instant τ_2.

The Hermitian conjugate of the first summand in the last equation is easily calculated by noting that the exact reduced propagator $\overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2)$, which actually propagates only the excited-state sector of the reduced density matrix, satisfies

$$A\overleftarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2)=\overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2)A, \tag{S50}$$

for arbitrary purely electronic operator A. Introducing the spontaneous emission rate Γ_x from excitonic state $|x\rangle$

$$\Gamma_x=\frac{1}{4\pi\varepsilon_0}\,\frac{4\omega_x^3\,|\boldsymbol{\mu}_x|^2}{3\hbar c^3}, \tag{S51}$$

the final result for the excited-state sector of the RDM in the interaction picture reads as

$$\begin{aligned}\rho_{ee}^{(I)}(t) = & \int_{t_0}^{t} \mathrm{d}\tau_2\, \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2) \times \\ & \times \sum_{\bar{x}x} \left[\frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_{\bar{x}}|^2} \frac{1}{2} \Gamma_{\bar{x}} n_{\mathrm{BE}}(\omega_{\bar{x}}, T_R) + \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_x|^2} \frac{1}{2} \Gamma_x n_{\mathrm{BE}}(\omega_x, T_R) \right] \mathrm{e}^{\mathrm{i}\omega_{\bar{x}}(\tau_2 - t_0)} |\bar{x}\rangle\langle x|\, \mathrm{e}^{-\mathrm{i}\omega_x(\tau_2 - t_0)}.\end{aligned} \tag{S52}$$

One can now formulate in the usual manner the HEOM that replaces Eq. (S52). In doing so, we immediately realize that only the equation of motion for RDM has the source term describing the generation of excitations from the ground state, while ADMs do not possess such a term. In greater detail, the interaction-picture ADM labeled by vector $\mathbf{n}$ assumes the form

$$\begin{aligned}\sigma_{ee,\mathbf{n}}^{(I)}(t) = & \int_{t_0}^{t} \mathrm{d}\tau_2\, T \left\{ \prod_j \prod_m \left[\int_{\tau_2}^{t} \mathrm{d}s\, \mathrm{e}^{-\mu_{j,m}(t-s)} \left(\mathrm{i}\frac{c_{j,m}^r}{\hbar^2} V_j^{(I)}(s)^\times - \frac{c_{j,m}^i}{\hbar^2} V_j^{(I)}(s)^\circ \right) \right]^{n_{j,m}} \overrightarrow{\mathcal{U}}_{\mathrm{red}}^{(I)}(t,\tau_2,\tau_2) \right\} \times \\ & \times \sum_{\bar{x}x} \left[\frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_{\bar{x}}|^2} \frac{1}{2} \Gamma_{\bar{x}} n_{\mathrm{BE}}(\omega_{\bar{x}}, T_R) + \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_x|^2} \frac{1}{2} \Gamma_x n_{\mathrm{BE}}(\omega_x, T_R) \right] \mathrm{e}^{\mathrm{i}\omega_{\bar{x}}(\tau_2 - t_0)} |\bar{x}\rangle\langle x|\, \mathrm{e}^{-\mathrm{i}\omega_x(\tau_2 - t_0)}\end{aligned} \tag{S53}$$

while its equation of motion reads as

$$\begin{aligned}\partial_t \sigma_{ee,\mathbf{n}}(t) = & -\frac{\mathrm{i}}{\hbar} \left[H_M, \sigma_{ee,\mathbf{n}}(t) \right] - \left(\sum_j \sum_m n_{j,m} \mu_{j,m} \right) \sigma_{ee,\mathbf{n}}(t) \\ & + \delta_{\mathbf{n},\mathbf{0}} \sum_{\bar{x}x} \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_{\bar{x}}|^2} \frac{1}{2} \Gamma_{\bar{x}} n_{\mathrm{BE}}(\omega_{\bar{x}}, T_R) |\bar{x}\rangle\langle x| + \delta_{\mathbf{n},\mathbf{0}} \sum_{\bar{x}x} \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_x|^2} \frac{1}{2} \Gamma_x n_{\mathrm{BE}}(\omega_x, T_R) |\bar{x}\rangle\langle x| \\ & + \mathrm{i} \sum_j \sum_m \left[V_j, \sigma_{ee,\mathbf{n}_{j,m}^+}(t) \right] + \mathrm{i} \sum_j \sum_m n_{j,m} \left(\frac{c_{j,m}}{\hbar^2} V_j \sigma_{ee,\mathbf{n}_{j,m}^-}(t) - \frac{c_{j,m}^*}{\hbar^2} \sigma_{ee,\mathbf{n}_{j,m}^-}(t) V_j \right).\end{aligned} \tag{S54}$$

In Eq. (S54), 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 photon occupation numbers. The rate at which the population of excitonic state $|x\rangle$ is generated from the ground state assumes the familiar form

$$\left(\partial_t n_{xx}(t) \right)_{\mathrm{source}} = \Gamma_x n_{\mathrm{BE}}(\omega_x, T_R), \tag{S55}$$

where the spontaneous emission rate Γ_x is multiplied by the Bose–Einsten 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 $|\bar{x}\rangle$ and $|x\rangle$ $(\bar{x} \neq x)$ is generated from the ground state contains factors $\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*$ describing the alignment of the corresponding transition dipole moments

$$\left(\partial_t n_{\bar{x}x}(t) \right)_{\mathrm{source}} = \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_{\bar{x}}|^2} \frac{1}{2} \Gamma_{\bar{x}} n_{\mathrm{BE}}(\omega_{\bar{x}}, T_R) + \frac{\boldsymbol{\mu}_{\bar{x}} \cdot \boldsymbol{\mu}_x^*}{|\boldsymbol{\mu}_x|^2} \frac{1}{2} \Gamma_x n_{\mathrm{BE}}(\omega_x, T_R). \tag{S56}$$

Interestingly, these source terms are present exclusively in the equation for the RDM, as indicated by the presence of the Kronecker delta $\delta_{\mathbf{n},\mathbf{0}}$. At first sight, this is very different from the description of the light–matter interaction on the quantum-optical level in, e.g., Ref. 14, which is inspired by the combined Born–Markov–HEOM approach developed in Ref. 15. There, each level of the hierarchy contains source terms similar to the ones we encounter in Eq. (S54) on the level of the RDM. Moreover, the quantum-optical source terms in Ref. 14 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, while the excited-state populations are at least quadratic in the weak exciting field and are much smaller than 1, compare to the scaling laws under semiclassical light–matter interactions [Eqs. (13)] presented in the main text. We have already used similar arguments in the main text to transform the HEOM that does not take into account scaling laws to the HEOM that is consistently up to the second order in the optical field. Here, on the quantum-optical level, the generation rate of excited-state populations, Eq. (S55), 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.

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