

Multistep Quantum Master Equation Theory for Response Functions in Four Wave Mixing Electronic Spectroscopy of Multichromophoric Macromolecules[†]

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This work provides an alternative derivation of third order response functions in four wave mixing spectroscopy of multichromophoric macromolecular systems considering only single exciton states. For the case of harmonic oscillator bath linearly and diagonally coupled to exciton states, closed form expressions showing all the explicit time dependences are derived. These expressions can provide more solid physical basis for understanding 2-dimensional electronic spectroscopy signals. For more general cases of system-bath coupling, the quantum master equation (QME) approach is employed for the derivation of multistep time evolution equations for Green function-like operators. Solution of these equations is feasible at the level of 2nd order non-Markovian QME, and the new approach can account for inter-exciton coupling, dephasing, relaxation, and non-Markovian effects in a consistent manner.

Key Words : Four wave mixing, Response function, Multichromophoric macromolecule

Introduction

Electronic excitation is the outcome of correlated motion of electrons and is fundamentally quantum mechanical. When they are put together at nanometer length scale, each excitation loses its individuality and coherent superposition of those excitations, excitons, can be formed. This is possible even without physical contacts between chromophores because of long range characteristics of Coulomb interactions in particular. Thus, the energetics and the dynamics of delocalized excitons in so called multichromophoric macromolecule (MCMM) often result in optical properties that are distinctively different from those of individual chromophores. Well known examples of such MCMMs are photosynthetic light harvesting complexes,¹⁻⁴ conjugated polymers,⁵⁻¹⁰ and dendrimers.¹¹⁻¹⁵ Excitons in these MCMMs are tunable but fragile, which are being utilized positively for efficient and robust collection/transfer of excitons in natural photosynthetic light harvesting complexes.¹⁶⁻¹⁹ Similar utilization in synthetic MCMMs, if possible, can lead to novel mechanisms of solar energy conversion^{20,21} and sensor development. Detailed spectroscopic studies of MCMM are needed to explore these possibilities.

In general, spectroscopic study of MCMM is difficult because of broad range of dynamical time scales and the large number of structural/energetic degrees of freedom. In understanding how their optical properties reflect the molecular level structural and dynamical details, conventional linear spectroscopy is severely limited. Nonlinear spectroscopy of MCMM has an important role to play in this regard.²²⁻²⁵ Indeed, recent progress in 2-dimensional electronic spectroscopy (2DES)²⁶⁻²⁹ made it possible to identify quantum coherence lasting up to

500 fs in photosynthetic light harvesting complexes despite significant amount of disorder and fluctuations. Theoretical modelings of these 2DES signals have been made,³⁰⁻³⁴ but clear understanding of the origins and effects of the coherent quantum beating is not available yet. This motivates the need for more advanced theoretical approaches that can provide reliable and efficient description of exciton dynamics in such MCMM systems. The formulation presented in this work provides an important basis for developing such theoretical approaches.

Hamiltonian

For a molecular system subject to an optical probe, the total matter-radiation Hamiltonian (within the semiclassical approximation of the radiation) is

$$H_T(t) = H + H_{int}(t), \quad (1)$$

where H is the material Hamiltonian representing the MCMM and its environment, and $H_{int}(t)$ represents the matter-radiation interaction. The material Hamiltonian can be expressed as

$$H \equiv \mathcal{E}_g |g\rangle\langle g| + H_e + H_{eb} + H_b, \quad (2)$$

where $|g\rangle$ is the ground electronic state with energy \mathcal{E}_g , H_e the exciton Hamiltonian, H_{eb} the exciton-bath Hamiltonian, and H_b the bath Hamiltonian. Here, the "bath" represents all other molecular and environmental degrees of freedom interacting with the excitons. Thus, when the molecule is in the ground electronic state, H reduces to

$$H_g = \mathcal{E}_g |g\rangle\langle g| + H_b. \quad (3)$$

When the molecules are electronically excited, H effectively becomes

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

$$H_{ex} = H_e + H_{eb} + H_b. \quad (4)$$

For simplicity, only single exciton states are considered here although consideration up to double exciton states may be necessary for full analysis of 2DES signals. In the site excitation basis, the exciton Hamiltonian has the following form:

$$H_e = \sum_l (E_l + \mathcal{E}_e) |l\rangle\langle l| + \sum_{l,l'} \Delta_{l,l'} |l\rangle\langle l'|, \quad (5)$$

where $|l\rangle$ is the state where only the l th chromophore is excited and $(E_l + \mathcal{E}_e)$ is its energy. In this definition, \mathcal{E}_e is a reference excitation energy of the MCM, which can be chosen to be the average of the excited state energies, the lowest exciton state, or any other value that can represent the average property of the excitons. Thus, E_l 's are values comparable to differences of excitation energies in the single exciton space. For later use, we introduce h_e as the exciton Hamiltonian without the contribution of \mathcal{E}_e as follows:

$$h_e = H_e - \mathcal{E}_e \sum_l |l\rangle\langle l| = \sum_l E_l |l\rangle\langle l| + \sum_{l,l'} \Delta_{l,l'} |l\rangle\langle l'|. \quad (6)$$

When diagonalized, the exciton Hamiltonian can be expressed as

$$H_e = \sum_j (\mathcal{E}_j + \mathcal{E}_e) |\varphi_j\rangle\langle \varphi_j|, \quad (7)$$

where $\mathcal{E}_j + \mathcal{E}_e$ is the energy of the exciton state $|\varphi_j\rangle$. Equivalently, this can be expressed as

$$h_e = \sum_j \mathcal{E}_j |\varphi_j\rangle\langle \varphi_j|. \quad (8)$$

Analogously, we can also define

$$h_{ex} = h_e + H_{eb} + H_b. \quad (9)$$

The unitary transformation matrix between the site basis and the exciton basis is denoted as U . The matrix elements of this transformation are defined as $U_{ij} = \langle l|\varphi_j\rangle$, and the following relation holds:

$$|l\rangle = \sum_{j=1}^N U_{lj}^* |\varphi_j\rangle. \quad (10)$$

The transition dipole vector for the excitation from $|g\rangle$ to $|l\rangle$ is denoted as $\boldsymbol{\mu}_l$. Then, the total electronic polarization operator for the transitions to the single exciton space of the MCM is given by

$$\begin{aligned} \mathbf{P} &= \sum_l \boldsymbol{\mu}_l (|l\rangle\langle g| + |g\rangle\langle l|) \\ &= \sum_l \sum_j (\boldsymbol{\mu}_l U_{lj}^* |\varphi_j\rangle\langle g| + |g\rangle\langle \varphi_j| U_{lj} \boldsymbol{\mu}_l) \\ &= \sum_j (\mathbf{D}_j |\varphi_j\rangle\langle g| + |g\rangle\langle \varphi_j| \mathbf{D}_j) \\ &= |\mathbf{D}\rangle\langle g| + |g\rangle\langle \mathbf{D}|, \end{aligned} \quad (11)$$

where $\mathbf{D}_j = \sum_l \boldsymbol{\mu}_l U_{lj}^*$ and $|\mathbf{D}\rangle \equiv \sum_j \mathbf{D}_j |\varphi_j\rangle$.

Assuming three incoming pulses, the matter-radiation interaction Hamiltonian is

$$\begin{aligned} H_{int}(t) &= \sum_{\alpha=1}^3 \mathbf{E}_{\alpha}(t-t_{\alpha}) \cdot |\mathbf{D}\rangle\langle g| e^{i\mathbf{k}_{\alpha} \cdot \mathbf{r} - i\omega_{\alpha} t} + \text{H.c.} \\ &= \sum_{\alpha=1}^3 \sum_j \mathbf{E}_{\alpha}(t-t_{\alpha}) \cdot \mathbf{D}_j |\varphi_j\rangle\langle g| e^{i\mathbf{k}_{\alpha} \cdot \mathbf{r} - i\omega_{\alpha} t} + \text{H.c.} \\ &= \sum_{\alpha=1}^3 \mathbf{E}_{\alpha}(t-t_{\alpha}) \cdot |\mathbf{D}_{\alpha}\rangle\langle g| e^{i\mathbf{k}_{\alpha} \cdot \mathbf{r} - i\omega_{\alpha} t} + \text{H.c.}, \end{aligned} \quad (12)$$

where $\mathbf{E}_{\alpha}(t-t_{\alpha})$ is the amplitude of the α th pulse with polarization vector $\boldsymbol{\varepsilon}_{\alpha}$. Thus, $\mathbf{E}_{\alpha}(t-t_{\alpha}) = E_{\alpha}(t-t_{\alpha}) \boldsymbol{\varepsilon}_{\alpha}$. It is assumed that $t_3 \geq t_2 \geq t_1$. In the last line of Eq. (12), $|\mathbf{D}_{\alpha}\rangle$ is the sum of all the exciton states weighted by the components of the transition dipoles along the direction $\boldsymbol{\varepsilon}_{\alpha}$ and has the following expression:

$$|\mathbf{D}_{\alpha}\rangle = \sum_j \boldsymbol{\varepsilon}_{\alpha} \cdot \mathbf{D}_j |\varphi_j\rangle \quad (13)$$

Response Functions

General Expressions. Assume that the optical field is active from $t=0$ and that the total density operator of the material at this time is $\rho(0) = |g\rangle\langle g| \rho_b$, where $\rho_b = e^{-\beta H_b} / \text{Tr}_b\{e^{-\beta H_b}\}$ with $\beta = 1/k_B T$. Thus $[\rho_b, H_b] = 0$. Then, the time evolution operator governing the total material system for $t > 0$ is given by

$$\mathcal{U}(t) = \exp_{(+)} \left\{ -\frac{i}{\hbar} \int_0^t dt' H_T(t') \right\}, \quad (14)$$

where (+) represents chronological time ordering. Then, the total density operator at time t_m is

$$\rho(t_m) = \mathcal{U}(t_m) \rho(0) \mathcal{U}^{\dagger}(t_m). \quad (15)$$

Expanding $\mathcal{U}(t)$ and $\mathcal{U}^{\dagger}(t)$ with respect to $H_{int}(t)$, and collecting all the terms of the third order, we find the following third order components of the density operator:

$$\rho^{(3)}(t_m) = \rho_I(t_m) + \rho_I^{\dagger}(t_m) + \rho_{II}(t_m) + \rho_{II}^{\dagger}(t_m), \quad (16)$$

where

$$\begin{aligned} \rho_I(t_m) &= -\frac{i}{\hbar^3} \int_0^{t_m} dt \int_0^t dt' \int_0^{t'} dt'' e^{-iH(t_m-t)/\hbar} \\ &\quad \times H_{int}(t) e^{-iH(t-t')/\hbar} H_{int}(t') e^{-iHt'/\hbar} \rho(0) \\ &\quad \times e^{iHt''/\hbar} H_{int}(t'') e^{iH(t_m-t'')/\hbar}, \end{aligned} \quad (17)$$

$$\begin{aligned} \rho_{II}(t_m) &= -\frac{i}{\hbar^3} \int_0^{t_m} dt \int_0^t dt' \int_0^{t'} dt'' e^{-iHt_m/\hbar} \rho(0) \\ &\quad \times e^{iHt''/\hbar} H_{int}(t'') e^{iH(t-t'')/\hbar} H_{int}(t') \\ &\quad \times e^{iH(t-t')/\hbar} H_{int}(t) e^{iH(t_m-t)/\hbar}. \end{aligned} \quad (18)$$

In Eq. (17), the integration over t'' can be split into obtain the following general expression: three regions, $0 < t'' < t'$, $t' < t'' < t$, and $t < t'' < t_m$. Relabeling the dummy time integration variables in each region such that $t \geq t' \geq t''$, the three terms can be rewritten so as to have the same time integration

boundaries as $\rho_I(t_m)$. The resulting third order components can be expressed as

$$\rho^{(3)}(t_m) = -\frac{i}{\hbar^3} \int_0^{t_m} dt \int_0^t dt' \int_0^{t'} dt'' \sum_{j=1}^4 T_j(t_m, t, t', t'') + \text{H.c.}, \quad (19)$$

where

$$T_1(t_m, t, t', t'') \equiv e^{-iH(t_m-t')/\hbar} H_{int}(t') e^{-iH(t'-t'')/\hbar} \times H_{int}(t'') e^{-iH''/\hbar} \rho(0) e^{iH'/\hbar} H_{int}(t) e^{iH(t_m-t)/\hbar}, \quad (20)$$

$$T_2(t_m, t, t', t'') \equiv e^{-iH(t_m-t)/\hbar} H_{int}(t) e^{-iH(t_m-t')/\hbar} \times H_{int}(t'') e^{-iH''/\hbar} \rho(0) e^{iH'/\hbar} H_{int}(t') e^{iH(t-t'')/\hbar}, \quad (21)$$

$$T_3(t_m, t, t', t'') \equiv e^{-iH(t_m-t)/\hbar} H_{int}(t) e^{-iH(t-t')/\hbar} \times H_{int}(t') e^{-iH''/\hbar} \rho(0) e^{iH'/\hbar} H_{int}(t'') e^{iH(t_m-t'')/\hbar}, \quad (22)$$

$$T_4(t_m, t, t', t'') \equiv e^{-iH''/\hbar} \rho(0) e^{iH''/\hbar} H_{int}(t'') \times e^{-iH(t'-t'')/\hbar} H_{int}(t') e^{iH(t-t')/\hbar} H_{int}(t) e^{iH(t_m-t)/\hbar}. \quad (23)$$

In the above expressions, Eqs. (20)-(22) come from $\rho_I(t_m)$ and Eq. (23) comes from $\rho_I(t_m)$.

The corresponding third order contribution to the polarization can be calculated by taking the trace of the where scalar product between \mathbf{P} , Eq. (11), and $\rho^{(3)}(t_m)$, Eq. (19). The resulting expression for the third order polarization at time t_m can be shown to be

$$\bar{\mathbf{P}}^{(3)}(t_m) \equiv Tr\{\mathbf{P}\rho^{(3)}(t_m)\} = \frac{2}{\hbar^3} \sum_{j=1}^4 \text{Im} \int_0^{t_m} dt \int_0^t dt' \int_0^{t'} dt'' Tr\{\mathbf{P}T_j(t_m, t, t', t'')\}, \quad (24)$$

where ‘‘Im’’ implies imaginary part of the complex function.

Denote the unit vector of the polarization being measured at time t_m as $\boldsymbol{\varepsilon}_m$. Taking scalar product of this with the integrand of Eq. (24) and considering only those terms where interactions with E_1 , E_2 , and E_3 occur in the chronological order at t'' , t' , and t , respectively, we obtain the following general expression:

$$\boldsymbol{\varepsilon}_m \cdot Tr\{\mathbf{P}T_1(t_m, t, t', t'')\} = E_3^*(t-t_3)E_2^*(t'-t_2) \times E_1(t''-t_1) e^{i(\omega_3 t + \omega_2 t' - \omega_1 t'')} e^{-i(\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} \times Tr_b \left\{ e^{-iH_g(t_m-t')/\hbar} \langle D_2 | e^{-iH_{ex}(t-t'')/\hbar} | D_1 \rangle \times \rho_b e^{iH_g(t-t'')/\hbar} \langle D_3 | e^{iH_{ex}(t_m-t)/\hbar} | D_4 \rangle \right\}, \quad (25)$$

$$\boldsymbol{\varepsilon}_m \cdot Tr\{\mathbf{P}T_2(t_m, t, t', t'')\} = E_3^*(t-t_3)E_2^*(t'-t_2) \times E_1(t''-t_1) e^{i(\omega_3 t + \omega_2 t' - \omega_1 t'')} e^{-i(\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} \times Tr_b \left\{ e^{-iH_g(t_m-t)/\hbar} \langle D_3 | e^{-iH_{ex}(t-t'')/\hbar} | D_1 \rangle \times \rho_b e^{iH_g(t'-t'')/\hbar} \langle D_2 | e^{iH_{ex}(t_m-t')/\hbar} | D_4 \rangle \right\}, \quad (26)$$

$$\boldsymbol{\varepsilon}_m \cdot Tr\{\mathbf{P}T_3(t_m, t, t', t'')\} = E_3^*(t-t_3)E_2^*(t'-t_2) \times E_1^*(t''-t_1) e^{i(\omega_3 t - \omega_2 t' + \omega_1 t'')} e^{-i(\mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_1) \cdot \mathbf{r}} \times Tr_b \left\{ e^{-iH_g(t_m-t)/\hbar} \langle D_3 | e^{-iH_{ex}(t-t'')/\hbar} | D_2 \rangle \times e^{-iH_g(t'-t'')/\hbar} \rho_b \langle D_1 | e^{iH_{ex}(t_m-t'')/\hbar} | D_4 \rangle \right\}, \quad (27)$$

$$\boldsymbol{\varepsilon}_m \cdot Tr\{\mathbf{P}T_4(t_m, t, t', t'')\} = E_3^*(t-t_3)E_2^*(t'-t_2) \times E_1^*(t''-t_1) e^{i(\omega_3 t - \omega_2 t' + \omega_1 t'')} e^{-i(\mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_1) \cdot \mathbf{r}} \times Tr_b \left\{ e^{-iH_g(t_m-t'')/\hbar} \rho_b \langle D_1 | e^{-iH_{ex}(t'-t'')/\hbar} | D_2 \rangle \times e^{iH_g(t-t'')/\hbar} \langle D_3 | e^{iH_{ex}(t_m-t)/\hbar} | D_4 \rangle \right\}. \quad (28)$$

where

$$|D_4\rangle = \sum_j \boldsymbol{\varepsilon}_m \cdot \mathbf{D}_j | \varphi_j \rangle \quad (29)$$

At this point, it is convenient to introduce new time variables, $\tau = t_m - t$, $T_p = t - t'$, and $\tau' = t' - t''$. As will be clear, these notations imply that τ and τ' are coherence times and that T_p is the population time. Replacing the time integration variables in Eq. (24) with these and taking scalar product of $\bar{\mathbf{P}}^{(3)}(t_m)$ with $\boldsymbol{\varepsilon}_m$, we obtain the following expression:

$$\boldsymbol{\varepsilon}_m \cdot \bar{\mathbf{P}}^{(3)}(t_m) = \frac{2}{\hbar^3} \sum_{j=1}^4 \text{Im} \int_0^{t_m} d\tau \int_0^{t_m-\tau} dT_p \int_0^{t_m-T_p-\tau} d\tau' \boldsymbol{\varepsilon}_m \cdot Tr\{\mathbf{P}T_j(t_m, t_m-\tau, t_m-\tau-T_p, t_m-\tau-T_p-\tau')\} \quad (30)$$

Inserting Eqs. (25)-(28) into Eq. (30)

$$\boldsymbol{\varepsilon}_m \cdot \bar{\mathbf{P}}^{(3)}(t_m) = 2 \text{Im} \int_0^{t_m} d\tau \int_0^{t_m-\tau} dT_p \int_0^{t_m-T_p-\tau} d\tau' \{ E_3^*(t_m-\tau-t_3)E_2^*(t_m-\tau-T_p-t_2) \times E_1(t_m-\tau-T_p-\tau'-t_1) e^{i(\omega_3+\omega_2-\omega_1)(t_m-\tau)} \times e^{-i(\omega_2-\omega_1)T_p} e^{i\omega_1\tau'} e^{i(\varepsilon_e-\varepsilon_g)(\tau-\tau')/\hbar} \times e^{-i(\mathbf{k}_3+\mathbf{k}_2-\mathbf{k}_1) \cdot \mathbf{r}} (\chi^{(1)}(\tau, T_p, \tau') + \chi^{(2)}(\tau, T_p, \tau')) + E_3^*(t_m-\tau-t_3)E_2^*(t_m-\tau-T_p-t_2) \times E_1^*(t_m-\tau-T_p-\tau'-t_1) e^{i(\omega_3-\omega_2+\omega_1)(t_m-\tau)} \times e^{i(\omega_2-\omega_1)T_p} e^{-i\omega_1\tau'} e^{i(\varepsilon_e-\varepsilon_g)(\tau+\tau')/\hbar} \times e^{-i(\mathbf{k}_3-\mathbf{k}_2+\mathbf{k}_1) \cdot \mathbf{r}} (\chi^{(3)}(\tau, T_p, \tau') + \chi^{(4)}(\tau, T_p, \tau')) \}, \quad (31)$$

where

$$\chi^{(1)}(\tau, T_p, \tau') = Tr_b \left\{ e^{-iH_b(\tau+T_p)/\hbar} \langle D_2 | e^{-ih_{ex}\tau/\hbar} | D_1 \rangle \times \rho_b e^{iH_b(T_p+\tau)/\hbar} \langle D_3 | e^{ih_{ex}\tau'/\hbar} | D_4 \rangle \right\}, \quad (32)$$

$$\chi^{(2)}(\tau, T_p, \tau') = Tr_b \left\{ e^{-iH_b\tau/\hbar} \langle D_3 | e^{-ih_{ex}(T_p+\tau)/\hbar} | D_1 \rangle \times \rho_b e^{iH_b\tau'/\hbar} \langle D_2 | e^{ih_{ex}(\tau+T_p)/\hbar} | D_4 \rangle \right\}, \quad (33)$$

$$\chi^{(3)}(\tau, T_p, \tau') = Tr_b \left\{ e^{-iH_b\tau/\hbar} \langle D_3 | e^{-ih_{ex}T_p/\hbar} | D_2 \rangle \times e^{-iH_b\tau'/\hbar} \rho_b \langle D_1 | e^{ih_{ex}(\tau+T_p+\tau')/\hbar} | D_4 \rangle \right\}, \quad (34)$$

$$\chi^{(4)}(\tau, T_p, \tau') = Tr_b \left\{ e^{-iH_b(\tau+T_p+\tau')/\hbar} \rho_b \times \langle D_1 | e^{ih_{ex}\tau'/\hbar} | D_2 \rangle e^{iH_bT_p/\hbar} \langle D_3 | e^{ih_{ex}\tau/\hbar} | D_4 \rangle \right\}. \quad (35)$$

The above general expressions for the response functions are equivalent to those in previous works^{22-25,28} within the assumption that only single exciton states contribute. Fourier transforms of these with respect to τ and τ' can be related to the spectra of 2DES if proper averaging over the ensemble of disorder is made.

Closed Form Expressions for Diagonal System-bath Coupling in the Exciton Basis. For the case where the bath Hamiltonian can be modeled by harmonic oscillators and the exciton-bath coupling is diagonal in the exciton basis and is linear in the displacements of harmonic oscillators, a simple closed-form expression can be found for each response function. Thus, suppose that $H_b = \sum_n \hbar \omega_n (b_n^\dagger b_n + 1/2)$, where b_n and b_n^\dagger are the lowering and raising operators of the n th oscillator, and that

$$H_{eb} = \sum_j \delta H_{bj} |\varphi_j\rangle \langle \varphi_j| = \sum_j \sum_n \hbar \omega_n g_{j,n} (b_n + b_n^\dagger) |\varphi_j\rangle \langle \varphi_j|, \quad (36)$$

Then, the four response functions defined by Eqs. (32)-(35) can be calculated explicitly. Explicit expressions for these can be derived based on generalized cumulant approach.³⁵ Alternatively, polaron displacement operator can be used as described in Appendix A. The resulting expressions are as follows.

$$\chi^{(1)}(\tau, T_p, \tau') = \sum_j \sum_{j'} D_{2,j}^* D_{1,j} D_{j',3}^* D_{j',4} e^{i\tilde{\epsilon}_j \tau/\hbar - i\tilde{\epsilon}_j \tau'/\hbar} \times e^{-\sum_n g_{j,n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n \tau)) - i \sin(\omega_n \tau) \right)}$$

$$\times e^{-\sum_n g_{j,n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n \tau)) - i \sin(\omega_n \tau) \right)} \times e^{-\sum_n g_{j,n} g_{j',n} \coth\left(\frac{\beta \hbar \omega_n}{2}\right) \{ \cos(\omega_n T_p) - \cos(\omega_n(\tau+T_p)) - \cos(\omega_n(T_p+\tau')) + \cos(\omega_n(\tau+T_p+\tau')) \}} \times e^{i \sum_n g_{j,n} g_{j',n} \{ \sin(\omega_n T_p) - \sin(\omega_n(\tau+T_p)) - \sin(\omega_n(T_p+\tau')) + \sin(\omega_n(\tau+T_p+\tau')) \}}, \quad (37)$$

$$\chi^{(2)}(\tau, T_p, \tau') = \sum_j \sum_{j'} D_{3,j}^* D_{1,j} D_{2,j'}^* D_{4,j'} e^{i\tilde{\epsilon}_j \tau/\hbar - i(\tilde{\epsilon}_j - \tilde{\epsilon}_{j'}) T_p/\hbar - i\tilde{\epsilon}_j \tau'/\hbar} \times e^{-\sum_n g_{j,n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n(T_p+\tau'))) - i \sin(\omega_n(T_p+\tau')) \right)} \times e^{-\sum_n g_{j',n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n(\tau+T_p))) + i \sin(\omega_n(\tau+T_p)) \right)} \times e^{-\sum_n g_{j,n} g_{j',n} \coth\left(\frac{\beta \hbar \omega_n}{2}\right) \{ \cos(\omega_n T_p) - \cos(\omega_n \tau) - \cos(\omega_n \tau') + \cos(\omega_n(\tau+T_p+\tau')) \}} \times e^{i \sum_n g_{j,n} g_{j',n} \{ -\sin(\omega_n T_p) - \sin(\omega_n \tau) - \sin(\omega_n \tau') + \sin(\omega_n(\tau+T_p+\tau')) \}}, \quad (38)$$

$$\chi^{(3)}(\tau, T_p, \tau') = \sum_j \sum_{j'} D_{3,j}^* D_{2,j} D_{1,j'}^* D_{4,j'} e^{i\tilde{\epsilon}_j(\tau+\tau')/\hbar - i(\tilde{\epsilon}_j - \tilde{\epsilon}_{j'}) T_p/\hbar} \times e^{-\sum_n g_{j,n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n T_p)) + i \sin(\omega_n T_p) \right)} \times e^{-\sum_n g_{j',n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n(\tau+T_p))) - i \sin(\omega_n(\tau+T_p+\tau')) \right)} \times e^{-\sum_n g_{j,n} g_{j',n} \coth\left(\frac{\beta \hbar \omega_n}{2}\right) \{ \cos(\omega_n T_p) - \cos(\omega_n \tau) - \cos(\omega_n \tau') + \cos(\omega_n(\tau+T_p)) \}} \times e^{i \sum_n g_{j,n} g_{j',n} \{ -\sin(\omega_n T_p) - \sin(\omega_n \tau) + \sin(\omega_n \tau') + \sin(\omega_n(\tau+T_p)) \}}, \quad (39)$$

$$\chi^{(4)}(\tau, T_p, \tau') = \sum_j \sum_{j'} D_{1,j} D_{2,j} D_{3,j'}^* D_{4,j'} e^{i\tilde{\epsilon}_j \tau/\hbar + i\tilde{\epsilon}_j \tau'/\hbar} \times e^{-\sum_n g_{j,n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n \tau)) - i \sin(\omega_n \tau) \right)} \times e^{-\sum_n g_{j',n}^2 \left(\coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(\omega_n \tau)) - i \sin(\omega_n \tau) \right)} \times e^{-\sum_n g_{j,n} g_{j',n} \coth\left(\frac{\beta \hbar \omega_n}{2}\right) \{ \cos(\omega_n(T_p+\tau')) - \cos(\omega_n \tau) - \cos(\omega_n \tau') + \cos(\omega_n(\tau+T_p)) \}} \times e^{i \sum_n g_{j,n} g_{j',n} \{ -\sin(\omega_n(T_p+\tau')) - \sin(\omega_n \tau) + \sin(\omega_n \tau') + \sin(\omega_n(\tau+T_p)) \}}, \quad (40)$$

In the above expressions, definitions of $D_{\alpha,j}$ and $\tilde{\epsilon}_j$ can be found in Eqs. (A5) and (A6).

Despite the simplicity of underlying assumption, the expressions shown in Eqs. (37)-(40) are quite complicated, which provide a glimpse of possible complications in reliable modeling of 2DES signals. First of all, it is obvious that the response functions cannot be simplified into products of linear-spectroscopic lineshape functions as long as there are common bath modes coupled to different exciton states. considering the delocalized nature of excitons, it would be extremely rare to find the case independent of each other. Second, terms oscillatory with respect to T_p can be found even in the absence of interexciton system-bath coupling. This is because transition to different exciton states is possible during the interaction with the pulse. This way, coherence between different exciton states can be maintained even in the absence of bath-mediated inter-exciton couplings.

Quantum Master Equation For General System-bath Coupling

Let us consider the general situation where the system-bath coupling and the bath Hamiltonian can be arbitrary. The quantum master equation (QME) approach^{36,37} can be employed to calculate these response functions in this case. First, using the cyclic symmetry within the trace operation and the fact that the exciton states commute with the bath Hamiltonian, Eqs. (32)-(35) can be recast into forms amenable for QME approach as follows:

$$\chi^{(1)}(\tau, T_p, \tau') = Tr_{b,e} \left\{ e^{-iH_b(\tau+T_p)/\hbar} |D_4\rangle\langle D_3| e^{-ih_{ex}\tau/\hbar} \times \rho_b |D_2\rangle\langle D_1| e^{iH_b(\tau+T_p)/\hbar} e^{ih_{ex}\tau/\hbar} \right\}, \quad (41)$$

$$\chi^{(2)}(\tau, T_p, \tau') = Tr_{b,e} \left\{ e^{-iH_b\tau/\hbar} |D_4\rangle\langle D_3| e^{-ih_{ex}(T_p+\tau)/\hbar} \times \rho_b |D_1\rangle\langle D_2| e^{iH_b\tau/\hbar} e^{ih_{ex}(\tau+T_p)/\hbar} \right\}, \quad (42)$$

$$\chi^{(3)}(\tau, T_p, \tau') = Tr_{b,e} \left\{ e^{-iH_b\tau/\hbar} |D_4\rangle\langle D_3| e^{-ih_{ex}T_p/\hbar} e^{-iH_b\tau'/\hbar} \times \rho_b |D_2\rangle\langle D_1| e^{ih_{ex}(\tau+T_p+\tau')/\hbar} \right\}, \quad (43)$$

$$\chi^{(4)}(\tau, T_p, \tau') = Tr_{b,e} \left\{ e^{-iH_b(\tau+T_p+\tau')/\hbar} \rho_b |D_4\rangle\langle D_1| \times e^{ih_{ex}\tau'/\hbar} e^{iH_bT_p/\hbar} |D_2\rangle\langle D_3| e^{ih_{ex}\tau/\hbar} \right\}. \quad (44)$$

Detailed methods to calculate these response functions based on the QME approach are described below.

Calculation of $\chi^{(1)}(\tau, T_p, \tau')$. For the calculation of $\chi^{(1)}(\tau, T_p, \tau')$, let us define

$$G_1^{(1)}(\tau') = e^{-ih_{ex}\tau'/\hbar} \rho_b |D_2\rangle\langle D_1| e^{iH_b\tau'/\hbar}, \quad (45)$$

$$G_2^{(1)}(T_p, \tau') = e^{-iH_bT_p/\hbar} G_1^{(1)}(\tau') e^{iH_bT_p/\hbar}, \quad (46)$$

$$G_3^{(1)}(\tau, T_p, \tau') = e^{-iH_b\tau/\hbar} |D_4\rangle\langle D_3| G_2^{(1)}(T_p, \tau') e^{ih_{ex}\tau/\hbar}. \quad (47)$$

Define $g_1^{(1)}(\tau')$, $g_2^{(1)}(T_p, \tau')$, and $g_3^{(1)}(\tau, T_p, \tau')$ as traces of $G_1^{(1)}(\tau')$, $G_2^{(1)}(T_p, \tau')$, and $G_3^{(1)}(\tau, T_p, \tau')$ over the bath degrees of freedom, respectively. Then,

$$\chi_3^{(1)}(\tau, T_p, \tau') = Tr_e \{ g_3^{(1)}(\tau, T_p, \tau') \}. \quad (48)$$

Unlike the conventional QME, three time arguments are involved in $g_3^{(1)}(\tau, T_p, \tau')$. The time evolution with respect to

τ can be considered first. Appendix B provides a detailed description. The resulting QME has an inhomogeneous term which in turn depends on the prior time evolutions during T_p and τ' . Different QMEs have to be derived for these as well. As can be seen in the Appendix B.1, explicit time evolution for T_p is not necessary for the present case. However, explicit time evolution with respect to τ' is needed. Appendix B. 1 provides formally exact QMEs for the following two reduced system operators:

$$\tilde{g}_1^{(1)}(\tau') = e^{ih_e\tau'/\hbar} g_1(\tau') \quad (49)$$

$$\tilde{g}_3^{(1)}(\tau, T_p, \tau') = g_3^{(1)}(\tau, T_p, \tau') e^{-ih_e\tau'/\hbar}. \quad (50)$$

Within the 2nd order approximation, all the time evolution operators involving $Q_L \tilde{H}_{eb}$ or $\tilde{H}_{eb} Q_R$ in Eqs. (B9) and (B11) can be disregarded. Thus, we obtain the following approximations:

$$\frac{d}{d\tau'} \tilde{g}_1^{(1)}(\tau') \approx -\frac{1}{\hbar^2} \int_0^{\tau'} ds Tr_b \{ \rho_b \tilde{H}_{eb}(s) \tilde{H}_{eb}(s) \} \tilde{g}_1^{(1)}(s), \quad (51)$$

$$\frac{d}{d\tau} \tilde{g}_3^{(1)}(\tau, T_p, \tau') = -\frac{1}{\hbar^2} |D_4\rangle\langle D_3| e^{-ih_e\tau'/\hbar} \times \int_0^{\tau'} ds Tr_b \{ \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(1)}(s) e^{iL_b(T_p+\tau')} \tilde{H}_{eb}(s) \} - \int_0^{\tau'} ds \tilde{g}_3^{(1)}(s, T_p, \tau') Tr_b \{ \rho_b \tilde{H}_{eb}(s) \tilde{H}_{eb}(s) \}. \quad (52)$$

The initial conditions for the above equations are $\tilde{g}_1^{(1)}(0) = |D_2\rangle\langle D_1|$ and $\tilde{g}_3^{(1)}(0, T_p, \tau') = |D_4\rangle\langle D_3| g_1^{(1)}(\tau')$.

Calculation of $\chi^{(2)}(\tau, T_p, \tau')$. For the calculation of $\chi^{(2)}(\tau, T_p, \tau')$ we define

$$G_1^{(2)}(\tau') \equiv e^{-ih_{ex}\tau'/\hbar} \rho_b |D_1\rangle\langle D_2| e^{iH_b\tau'/\hbar} \quad (53)$$

$$G_2^{(2)}(T_p, \tau') \equiv e^{-ih_{ex}T_p/\hbar} G_1^{(2)}(\tau') e^{ih_{ex}T_p/\hbar} \quad (54)$$

$$G_3^{(2)}(\tau, T_p, \tau') \equiv e^{-iH_b\tau/\hbar} |D_4\rangle\langle D_3| G_2^{(2)}(T_p, \tau') e^{ih_{ex}\tau/\hbar} \quad (55)$$

The traces of these operators over the bath degrees of freedom are respectively defined as $g_1^{(2)}(\tau')$, $g_2^{(2)}(T_p, \tau')$, and $g_3^{(2)}(\tau, T_p, \tau')$. Then,

$$\chi^{(2)}(\tau, T_p, \tau') = Tr_e \{ g_3^{(2)}(\tau, T_p, \tau') \} \quad (56)$$

Explicit time evolution with respect to all of τ , T_p , and τ' are necessary in the present case. Appendix B. 2 provides exact QMEs for the following interaction picture system operators:

$$\tilde{g}_1^{(2)}(\tau') = e^{ih_e\tau'/\hbar} g_1^{(2)}(\tau') \quad (57)$$

$$\tilde{g}_2^{(2)}(T_p, \tau') = e^{ih_eT_p/\hbar} g_2^{(2)}(T_p, \tau') e^{-ih_eT_p/\hbar} \quad (58)$$

$$\tilde{g}_3^{(2)}(\tau, T_p, \tau') = g_3^{(2)}(\tau, T_p, \tau') e^{-ih_e\tau/\hbar} \quad (59)$$

Up to the 2nd order of \tilde{H}_{eb} , the formally exact QMEs, Eqs. (B13), (B17), and (B19), can be approximated as

$$\frac{d}{d\tau} \tilde{g}_1^{(2)}(\tau) \approx -\frac{1}{\hbar^2} \int_0^\tau ds Tr_b \{ \rho_b \tilde{H}_{eb}(\tau) \tilde{H}_{eb}(s) \} \tilde{g}_1^{(2)}(s), \quad (60)$$

$$\frac{d}{dT_p} \tilde{g}_2^{(2)}(T_p, \tau) \approx \tilde{I}_2^{(2)}(T_p, \tau) - \int_0^{T_p} ds Tr_b \{ \tilde{\mathcal{L}}_{eb}(T_p) \tilde{\mathcal{L}}_{eb}(s) \rho_b \} \tilde{g}_2^{(2)}(s, \tau) \quad (61)$$

where

$$\tilde{I}_2^{(2)}(T_p, \tau) \approx -\frac{1}{\hbar^2} \int_0^\tau ds Tr_b \{ \tilde{\mathcal{L}}_{eb}(T_p) e^{-i\mathcal{L}_b \tau} \times e^{-iH_e \tau / \hbar} \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(2)}(s) \}, \quad (62)$$

and

$$\frac{d}{d\tau} \tilde{g}_3^{(2)}(\tau, T_p, \tau) \approx \tilde{I}_3^{(2)}(\tau, T_p, \tau) - \frac{1}{\hbar^2} \int_0^\tau ds \tilde{g}_3^{(2)}(s, T_p, \tau) Tr_b \{ \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \rho_b \} \quad (63)$$

with

$$\tilde{I}_3^{(2)}(\tau, T_p, \tau) \approx \frac{1}{\hbar^2} \int_0^\tau ds Tr_b \left\{ \left(e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} \times e^{-i\mathcal{L}_b \tau} e^{-iH_e \tau / \hbar} \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(2)}(s) \right) \tilde{H}_{eb}(\tau) \right\} + \frac{1}{\hbar} \int_0^{T_p} ds Tr_b \left\{ \left(e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} \tilde{\mathcal{L}}_{eb}(s) \tilde{g}_2(s, \tau) \rho_b \right) \times \tilde{H}_{eb}(\tau) \right\}. \quad (64)$$

The initial conditions are such that $\tilde{g}_3^{(2)}(0, T_p, \tau) = |D_4\rangle\langle D_3|g_2(T_p, \tau)$, $\tilde{g}_2^{(2)}(0, \tau) = g_1^{(2)}(\tau)$ and $g_1^{(2)}(0) = |D_1\rangle\langle D_2|$.

Calculation of $\chi^{(3)}(\tau, T_p, \tau)$. For the calculation of $\chi^{(3)}(\tau, T_p, \tau)$, we can define

$$G_1^{(3)}(\tau) \equiv e^{-iH_b \tau / \hbar} \rho_b |D_2\rangle\langle D_1| e^{-iH_{ex} \tau / \hbar}, \quad (65)$$

$$G_2^{(3)}(T_p, \tau) \equiv e^{-iH_{ex} T_p / \hbar} G_1^{(3)}(\tau) e^{iH_{ex} T_p / \hbar}, \quad (66)$$

$$G_3^{(3)}(\tau, T_p, \tau) \equiv e^{-iH_b \tau / \hbar} |D_4\rangle\langle D_3| G_2^{(3)}(T_p, \tau) e^{iH_{ex} \tau / \hbar}. \quad (67)$$

The traces of these operators over the bath degrees of freedom are respectively defined as $g_1^{(3)}(\tau)$, $g_2^{(3)}(T_p, \tau)$, and $g_3^{(3)}(\tau, T_p, \tau)$. Then,

$$\chi^{(3)}(\tau, T_p, \tau) = Tr_e \{ g_3^{(3)}(\tau, T_p, \tau) \}. \quad (68)$$

Three coupled equations are needed in this case as well. Appendix B.3 provides exact QMEs for

$$\tilde{g}_1^{(3)}(\tau) = g_1^{(3)}(\tau) e^{-iH_e \tau / \hbar}, \quad (69)$$

$$\tilde{g}_2^{(3)}(T_p, \tau) = e^{iH_e T_p / \hbar} g_2^{(3)}(T_p, \tau) e^{-iH_e T_p / \hbar}, \quad (70)$$

$$\tilde{g}_3^{(3)}(\tau, T_p, \tau) = g_3^{(3)}(\tau, T_p, \tau) e^{-iH_e \tau / \hbar}. \quad (71)$$

Up to the second order of \tilde{H}_{eb} , the exact QMEs, Eqs. (B26), (B30), and (B32), can be approximated as

$$\frac{d}{d\tau} \tilde{g}_1^{(3)}(\tau) \approx -\frac{1}{\hbar^2} \int_0^\tau ds \tilde{g}_1^{(3)}(s) Tr_b \{ \rho_b \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \}, \quad (72)$$

$$\frac{d}{dT_p} \tilde{g}_2^{(3)}(T_p, \tau) \approx \tilde{I}_2^{(3)}(T_p, \tau) - \int_0^{T_p} ds Tr_b \{ \tilde{\mathcal{L}}_{eb}(T_p) \tilde{\mathcal{L}}_{eb}(s) \rho_b \} \tilde{g}_2^{(3)}(s, \tau), \quad (73)$$

where

$$\tilde{I}_2^{(3)}(T_p, \tau) \approx -\frac{1}{\hbar} \int_0^\tau ds Tr_b \left\{ \tilde{\mathcal{L}}_{eb}(T_p) e^{-i\mathcal{L}_b \tau} e^{-iH_e \tau / \hbar} \times \rho_b \tilde{g}_1^{(3)}(s) \tilde{H}_{eb}(s) \right\}, \quad (74)$$

and

$$\frac{d}{d\tau} \tilde{g}_3^{(3)}(\tau, T_p, \tau) \approx \tilde{I}_3^{(3)}(\tau, T_p, \tau) - \frac{1}{\hbar^2} \int_0^\tau ds \tilde{g}_3^{(3)}(s, T_p, \tau) Tr_b \{ \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \rho_b \}, \quad (75)$$

with

$$\tilde{I}_3^{(3)}(\tau, T_p, \tau) \approx \frac{1}{\hbar^2} \int_0^\tau ds Tr_b \left\{ e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} \times e^{-i\mathcal{L}_b \tau} e^{-iH_e \tau / \hbar} \rho_b \tilde{g}_1^{(3)}(s) \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \right\} + \frac{1}{\hbar} \int_0^{T_p} ds Tr_b \left\{ \left(e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} \tilde{\mathcal{L}}_{eb}(s) \tilde{g}_2^{(3)}(s, \tau) \rho_b \right) \times \tilde{H}_{eb}(\tau) \right\}. \quad (76)$$

The initial conditions for the above equations are $\tilde{g}_3^{(3)}(0, T_p, \tau) = |D_4\rangle\langle D_3|g_2^{(3)}(T_p, \tau)$, $\tilde{g}_2^{(3)}(0, \tau) = g_1^{(3)}(\tau)$, and $g_1^{(3)}(0) = |D_2\rangle\langle D_1|$.

Calculation of $\chi^{(4)}(\tau, T_p, \tau)$. For the calculation of $\chi^{(4)}(\tau, T_p, \tau)$, we can define

$$G_1^{(4)}(\tau) \equiv e^{-iH_b \tau / \hbar} \rho_b |D_4\rangle\langle D_1| e^{iH_{ex} \tau / \hbar} \quad (77)$$

$$G_2^{(4)}(T_p, \tau) \equiv e^{-iH_b T_p / \hbar} G_1^{(4)}(\tau) e^{iH_b T_p / \hbar} \quad (78)$$

$$G_3^{(4)}(\tau, T_p, \tau) \equiv e^{-iH_b \tau / \hbar} G_2^{(4)}(T_p, \tau) |D_2\rangle\langle D_3| e^{iH_{ex} \tau / \hbar} \quad (79)$$

The traces of these operators over the bath degrees of freedom are respectively denoted as $g_1^{(4)}(\tau)$, $g_2^{(4)}(T_p, \tau)$, and $g_3^{(4)}(\tau, T_p, \tau)$. Then,

$$\chi^{(4)}(\tau, T_p, \tau) = Tr_e \{ g_3^{(4)}(\tau, T_p, \tau) \} \quad (80)$$

As in the case of $\chi^{(1)}(\tau, T_p, \tau)$ explicit time evolutions are necessary only for τ and τ' . Appendix B. 4 provides the exact

QMEs for

$$\tilde{g}_1^{(4)}(\tau) = g_1^{(4)}(\tau) e^{-ih_e \tau / \hbar}, \quad (81)$$

$$\tilde{g}_3^{(4)}(\tau, T_p, \tau') = g_3^{(4)}(\tau, T_p, \tau') e^{-ih_e \tau / \hbar}. \quad (82)$$

Within the 2nd order approximation, all the time evolution operators involving $Q_L \tilde{H}_{eb}$ or $\tilde{H}_{eb} Q_R$ can be disregarded in Eqs. (B41) and (B43). Thus, we obtain the following approximations:

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_1^{(4)}(\tau) \approx \\ -\frac{1}{\hbar^2} \int_0^\tau ds \tilde{g}_1^{(4)}(s) Tr_b \{ \rho_b \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \}, \end{aligned} \quad (83)$$

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_3^{(4)}(\tau, T_p, \tau') = & -\frac{1}{\hbar^2} \int_0^\tau ds Tr_b \{ (\rho_b g_1^{(4)}(s) \tilde{H}_{eb}(s) \\ & \times e^{ih_e \tau / \hbar} |D_2\rangle \langle D_3|) e^{iL_b(T_p + \tau)} \tilde{H}_{eb}(\tau) \} \\ & - \int_0^\tau ds \tilde{g}_3^{(1)}(s, T_p, \tau') Tr_b \{ \rho_b \tilde{H}_{eb}(s) \tilde{H}_{eb}(\tau) \}. \end{aligned} \quad (84)$$

The initial conditions are such that $\tilde{g}_1^{(4)}(0) = |D_4\rangle \langle D_1|$ and $\tilde{g}_3^{(4)}(0, T_p, \tau') = g_1^{(4)}(\tau') |D_2\rangle \langle D_3|$. These conclude the derivation of all the multistep QMEs necessary for the calculation of response functions.

Conclusion

This work provided a general formalism of four wave mixing spectroscopy of MCM systems, and developed a new multistep QME approach for the calculation of third order response functions. The consideration was limited to single exciton states only, but this was not due to fundamental limitation of the formalism but in order to present the main idea in its simplest form. Thus, extension of the present work to include double exciton states is possible, which will be considered in the future. In addition, explicit expressions for the response functions were derived for harmonic oscillator bath diagonally coupled to exciton states. While this result is not new, its derivation based on polaron displacement operator is new. The value of this derivation is more heuristic than practical, but it provides important insights for developing approximations for more challenging cases with off-diagonal exciton-bath coupling.

As was stated in the Introduction, the motivation of the present work was to develop an efficient and reliable computational methods that allow quantitative modeling of modern 2DES spectroscopy. For an MCM system where dephasing of exciton states due to diagonal exciton-bath couplings are the dominant mechanisms of line broadening, the results presented in Sec. III.B already serve that role. The expressions for the response functions remain valid for any kind of spectral densities with or without correlations among different site excitation or delocalized exciton states. In addition, averaging of that expression over an ensemble of the disorder

is possible at least numerically, which allows more quantitative assessment of homogeneous or inhomogeneous broadening mechanisms of detailed 2DES signals.

Section IV amounts to the main result of the present work. The multistep QMEs can describe inter-exciton transitions due to bath-mediated coupling as well as radiation induced ones in a consistent manner while including all the effects of dephasing and relaxation mechanisms. The complicated forms of the QMEs reflect the physical nature of the problem. Multiple matter-radiation interactions alter the Hamiltonian governing the system during time intervals in-between, which are represented by different QMEs. However, memory effects of the bath are sustained across the matter-radiation interactions, which are taken care of by inhomogeneous terms.

While the complete derivation of multistep QMEs was a significant step forward, much work still need to be done to establish it as a general methodology. As was indicated in the beginning of this section, generalization of this approach to include double exciton states is necessary. Numerical tests for simple model systems are also important in order to understand what are the unique features that can be explained by the multistep QMEs. Given that these objectives are accomplished, the formalism of the present work can serve as an attractive theoretical tool for quantitative analysis of various 2DES results for MCM systems.

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Appendix A: Derivation of Response Functions for Diagonal Exciton-bath Coupling

Consider the first response function $\chi^{(1)}(\tau, T_p, \tau')$ given by Eq. (32). For the case where the exciton-bath coupling is diagonal in the exciton basis as shown in Eq. (36), $e^{-ih_{ex} \tau / \hbar}$ and $e^{ih_{ex} \tau' / \hbar}$ can be expanded in the basis of $|\varphi_j\rangle$'s. The resulting expression is

$$\begin{aligned} \chi^{(1)}(\tau, T_p, \tau') = & \sum_j \sum_{j'} Tr_b \left\{ e^{-iH_b(\tau + T_p) / \hbar} \langle D_2 | \varphi_j \rangle \right. \\ & \times e^{-i(\epsilon_j + \delta H_{bj} + H_b) \tau / \hbar} \langle \varphi_j | D_1 \rangle \rho_b e^{iH_b(T_p + \tau') / \hbar} \\ & \left. \langle D_3 | \varphi_{j'} \rangle e^{i(\epsilon_{j'} + \delta H_{bj'} + H_b) \tau' / \hbar} \langle \varphi_{j'} | D_4 \rangle \right\}, \end{aligned} \quad (A1)$$

Let us introduce the following generator of polaron transformation for the exciton state j :

$$S_j = -\sum_n g_{j,n} (b_n - b_n^\dagger) \quad (A2)$$

Then, one can show that

$$e^{S_j(H_b + \delta H_{bj})} e^{-S_j} = H_b - \sum_n g_{j,n}^2 \hbar \omega_n \quad (A3)$$

In Eq. (A1), inserting $1 = e^{-S_j} e^{S_j}$ before and after $e^{-i(\epsilon_j + \delta H_{bj} + H_b)\tau/\hbar}$, we find the following expression:

$$\begin{aligned} \chi^{(1)}(\tau, T_p, \tau') &= \sum_j \sum_{j'} D_{2,j}^* D_{1,j} D_{3,j'}^* D_{4,j'} \\ &\times e^{-i\tilde{\epsilon}_j \tau/\hbar + i\tilde{\epsilon}_{j'} \tau'/\hbar} Tr_b \{ e^{-S_j(T_p + \tau)} \\ &\times e^{S_j(\tau + T_p + \tau')} e^{-S_j(\tau')} e^{S_j} \rho_b \}, \end{aligned} \quad (A4)$$

where

$$D_{\alpha,j} = \langle \varphi_j | D_{\alpha} \rangle, \quad (A5)$$

$$\tilde{\epsilon}_j = \epsilon_j - \sum_n g_{j,n}^2 \hbar \omega_n, \quad (A6)$$

$$S_j(\tau) = -\sum_n g_{j,n} (b_n e^{-i\omega_n \tau} - b_n^\dagger e^{i\omega_n \tau}). \quad (A7)$$

In deriving Eq. (A4), the following identity has been used:

$$e^{iH_b \tau/\hbar} e^{\pm S_j} e^{-iH_b \tau/\hbar} = e^{\pm S_j(\tau)}. \quad (A8)$$

The product of four displacement operators with different time arguments in Eq. (A4) can be calculated using the $e^A e^B = e^{A+B} e^{[A,B]/2}$, an identity that holds between any operator A and B as long as $[A, B]$ commutes with A and B . In fact, the following general identity can be established:

$$\begin{aligned} &Tr_b \{ e^{-S_j(x)} e^{S_j(x')} e^{-S_j(y)} e^{S_j(y')} \rho_b \} \\ &= e^{-\sum_n g_{jn}^2 \left\{ \coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(w_n(x-x'))) + i \sin(w_n(x-x')) \right\}} \\ &\times e^{-\sum_n g_{jn}^2 \left\{ \coth\left(\frac{\beta \hbar \omega_n}{2}\right) (1 - \cos(w_n(y-y'))) + i \sin(w_n(y-y')) \right\}} \\ &\times e^{-\sum_n g_{jn} g_{jn'} \coth\left(\frac{\beta \hbar \omega_n}{2}\right) \{ \cos(w_n(x-y)) - \cos(w_n(x'-y)) - \cos(w_n(x-y')) - \cos(w_n(x'-y')) \}} \\ &\times e^{i \sum_n g_{jn} g_{jn'} \{ \sin(w_n(x-y)) - \sin(w_n(x'-y)) - \sin(w_n(x-y')) + \sin(w_n(x'-y')) \}} \end{aligned} \quad (A9)$$

Application of the above identity to Eq. (A4) leads to Eq. (37).

For other response functions, similar manipulations lead to the following expressions:

$$\begin{aligned} \chi^{(2)}(\tau, T_p, \tau') &= \sum_j \sum_{j'} D_{3,j}^* D_{1,j} D_{2,j'}^* D_{4,j'} \\ &\times e^{-i\tilde{\epsilon}_j(T_p + \tau)/\hbar + i\tilde{\epsilon}_{j'}(\tau + T_p)/\hbar} Tr_b \{ e^{-S_j(\tau')} \\ &\times e^{S_j(\tau + T_p + \tau')} e^{-S_j(T_p + \tau')} e^{S_j} \rho_b \}, \end{aligned} \quad (A10)$$

$$\begin{aligned} \chi^{(3)}(\tau, T_p, \tau') &= \sum_j \sum_{j'} D_{3,j}^* D_{2,j} D_{1,j'}^* D_{4,j'} \\ &\times e^{-i\tilde{\epsilon}_j \tau/\hbar + i\tilde{\epsilon}_{j'}(\tau + T_p + \tau')/\hbar} Tr_b \{ e^{-S_j} \\ &\times e^{S_j(\tau + T_p + \tau')} e^{-S_j(T_p + \tau')} e^{S_j(\tau')} \rho_b \} \end{aligned} \quad (A11)$$

$$\begin{aligned} \chi^{(4)}(\tau, T_p, \tau') &= \sum_j \sum_{j'} D_{1,j}^* D_{2,j} D_{3,j'}^* D_{4,j'} \\ &\times e^{i\tilde{\epsilon}_j \tau' + i\tilde{\epsilon}_{j'} \tau/\hbar} Tr_b \{ e^{-S_j} e^{S_j(\tau')} \\ &\times e^{-S_j(T_p + \tau')} e^{S_j(\tau + T_p + \tau')} \rho_b \}, \end{aligned} \quad (A12)$$

Application of Eq. (A9) to the above expressions lead to Eqs. (38)-(40).

Appendix B: Derivation of Quantum Master Equations for General System-bath Coupling

1. Equations for $\chi^{(1)}(\tau, \tau', \tau'')$. First, define

$$\begin{aligned} \tilde{G}_3^{(1)}(\tau, T_p, \tau') &\equiv e^{iH_b \tau/\hbar} G_3^{(1)}(\tau, T_p, \tau') e^{-iH_b \tau/\hbar} e^{-i\mathcal{L}_e \tau/\hbar} \\ &= e^{i\mathcal{L}_b \tau} G_3^{(1)}(\tau, T_p, \tau') e^{-i\mathcal{L}_e \tau/\hbar}, \end{aligned} \quad (B1)$$

where $\mathcal{L}(\cdot) = [H_b(\cdot)]/\hbar$. Then,

$$\frac{d}{d\tau} \tilde{G}_3^{(1)}(\tau, T_p, \tau') = \frac{i}{\hbar} \tilde{G}_3^{(1)}(\tau, T_p, \tau') \tilde{H}_{eb}(\tau), \quad (B2)$$

where

$$\begin{aligned} \tilde{H}_{eb}(\tau) &\equiv e^{i\mathcal{L}_e \tau/\hbar} e^{iH_b \tau/\hbar} H_{eb} e^{-iH_b \tau/\hbar} e^{-i\mathcal{L}_e \tau/\hbar} \\ &= e^{i\mathcal{L}_b \tau} e^{i\mathcal{L}_e \tau} H_{eb}. \end{aligned} \quad (B3)$$

We introduce a right-hand side projection operator such that $(\cdot)\mathcal{P}_R = \rho_b Tr_b \{ \cdot \}$ and $\mathcal{Q}_R = 1 - \mathcal{P}_R$. Then, solving for $\tilde{G}_3^{(1)}(\tau, T_p, \tau') \mathcal{Q}_R$ and inserting this into the time evolution equation of $\tilde{G}_3^{(1)}(\tau, T_p, \tau') \mathcal{P}_R$, we find that

$$\begin{aligned} &\frac{d}{d\tau} \tilde{g}_3^{(1)}(\tau, T_p, \tau') = \\ &\frac{i}{\hbar} Tr_b \left\{ \tilde{G}_3^{(1)}(0, T_p, \tau') \mathcal{Q}_R e^{(-)} \int_0^\tau ds \tilde{H}_{eb}(s) \mathcal{Q}_R \tilde{H}_{eb}(\tau) \right\} \\ &- \int_0^\tau ds \tilde{g}_3^{(1)}(s, T_p, \tau') \\ &\times Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R e^{(-)} \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R \tilde{H}_{eb}(\tau') \right\} \end{aligned} \quad (B4)$$

where

$$\begin{aligned} \tilde{g}_3^{(1)}(0, T_p, \tau') &= |D_4\rangle \langle D_3 | Tr_b \{ G_1^{(1)}(\tau') \} \\ &\equiv |D_4\rangle \langle D_3 | g_1^{(1)}(\tau'), \end{aligned} \quad (B5)$$

$$\begin{aligned} \tilde{G}_3^{(1)}(0, T_p, \tau') \mathcal{Q}_R &= |D_4\rangle \langle D_3 | (e^{-i\mathcal{L}_b T_p} G_1^{(1)}(\tau')) \mathcal{Q}_R \\ &= |D_4\rangle \langle D_3 | e^{-i\mathcal{L}_b T_p} (G_1^{(1)}(\tau') \mathcal{Q}_R) \end{aligned} \quad (B6)$$

Thus, solution of Eq. (B4) requires information on $g_1^{(1)}(\tau')$, which can be obtained from $G_1^{(1)}(\tau') \mathcal{P}_R$, and that on $G_1^{(1)}(\tau') \mathcal{Q}_R$. The time evolutions for these can be obtained by employing a similar procedure. Defining a similar interaction picture

for $\tilde{G}_1^{(1)}(\tau)$

$$\tilde{G}_1^{(1)}(\tau) = e^{ih_e\tau/\hbar} e^{iL_b\tau} G_1(\tau) \quad (B7)$$

Then, employing a left hand projection operator \mathcal{P}_L defined by $\mathcal{P}_L(\cdot) \equiv \rho_b \text{Tr}_b\{\cdot\}$ and $\mathcal{Q}_L = 1 - \mathcal{P}_L$, and using the fact that $\mathcal{Q}_L \tilde{G}_1(0) = 0$, we obtain the following equations:

$$\begin{aligned} \mathcal{Q}_L \tilde{G}_1^{(1)}(\tau) &= -\frac{i}{\hbar} \int_0^\tau ds e_{(+)}^{-i} \int_0^s ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \\ &\times \mathcal{Q}_L \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(1)}(s) \end{aligned} \quad (B8)$$

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_1^{(1)}(\tau) &= -\frac{i}{\hbar^2} \int_0^\tau ds \text{Tr}_b\{\rho_b \tilde{H}_{eb}(\tau)\} \\ &\times e_{(+)}^{-i} \int_s^\tau ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \mathcal{Q}_L \tilde{H}_{eb}(s) \tilde{g}_1^{(1)}(s). \end{aligned} \quad (B9)$$

Combining Eqs. (B6), (B7), and (B8), we find that

$$\begin{aligned} \tilde{G}_3^{(1)}(0, T_p, \tau) \mathcal{Q}_R &= -\frac{i}{\hbar} |D_4\rangle \langle D_3| e^{-iL_b(T_p+\tau)} e^{-ih_e\tau/\hbar} \\ &\times \int_0^\tau ds e_{(+)}^{-i} \int_s^\tau ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(1)}(s), \end{aligned} \quad (B10)$$

where the fact that $G_1^{(1)}(\tau) \mathcal{Q}_R = \mathcal{Q}_L G_1^{(1)}(\tau)$ has been used. Inserting this into Eq. (B4), we find that

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_3^{(1)}(\tau, T_p, \tau) &= -\frac{1}{\hbar^2} |D_4\rangle \langle D_3| e^{-ih_e\tau/\hbar} \\ &\times \int_0^\tau ds \text{Tr}_b \left\{ e_{(+)}^{-i} \int_s^\tau ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(1)}(s) \right\} \\ &\times e^{iL_b(T_p+\tau)} e_{(-)}^{-i} \int_0^\tau ds \tilde{H}_{eb}(s) \mathcal{Q}_R \tilde{H}_{eb}(\tau) \left. \right\} \\ &- \int_0^\tau ds \tilde{g}_3^{(1)}(s, T_p, \tau) \\ &\times \text{Tr}_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{-i} \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R \tilde{H}_{eb}(\tau) \right\}, \end{aligned} \quad (B11)$$

Equations (B8), (B9), and (B11) form a closed set of equations that can be used to determine $\tilde{g}_3^{(1)}(\tau, T_p, \tau)$ starting from the initial condition, $g_1^{(1)}(0) = |D_2\rangle \langle D_1|$. These equations are exact but impractical because calculation of the unprojected part is difficult to obtain. Approximations of these equations up to the second order of \tilde{H}_{eb} are provided in the main text.

2. Equations for $\chi^{(2)}(\tau, T_p, \tau')$. Define

$$\tilde{G}_3^{(2)}(\tau, T_p, \tau') = e^{iL_b\tau} G_3^{(2)}(\tau, T_p, \tau') e^{-ih_e\tau/\hbar}. \quad (B12)$$

Then, $\tilde{g}_3(\tau, T_p, \tau') = \text{Tr}_b\{\tilde{G}_3^{(2)}(\tau, T_p, \tau')\}$. The equation governing the time evolution of $\tilde{g}_3^{(2)}(\tau, T_p, \tau')$ is the same as $\tilde{g}_3^{(1)}(\tau, T_p, \tau')$ except for the difference in the initial condition. Thus,

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_3^{(2)}(\tau, T_p, \tau') &= \\ &\frac{i}{\hbar} \text{Tr}_b \left\{ \tilde{G}_2^{(3)}(0, T_p, \tau') \mathcal{Q}_R e_{(-)}^{-i} \int_0^\tau ds \tilde{H}_{eb}(s) \mathcal{Q}_R \tilde{H}_{eb}(\tau) \right\} \\ &- \int_0^\tau ds \tilde{g}_3^{(2)}(s, T_p, \tau') \\ &\times \text{Tr}_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{-i} \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R \tilde{H}_{eb}(\tau) \right\}, \end{aligned} \quad (B13)$$

where

$$\begin{aligned} \tilde{G}_3^{(2)}(0, T_p, \tau') &= |D_4\rangle \langle D_3| \text{Tr}_b\{G_2^{(2)}(T_p, \tau')\} \\ &= |D_4\rangle \langle D_3| g_2^{(2)}(T_p, \tau') \end{aligned} \quad (B14)$$

$$\tilde{G}_3^{(2)}(0, T_p, \tau') \mathcal{Q}_R = |D_4\rangle \langle D_3| G_2^{(2)}(T_p, \tau') \mathcal{Q}_R \quad (B15)$$

Unlike the previous case, one has to solve explicitly the time evolution equations for $G_2^{(2)}(T_p, \tau')$. Employing the left projection operator $\mathcal{P}_L(\cdot) = \rho_b \text{Tr}_b\{\cdot\}$ and $\mathcal{Q}_L = 1 - \mathcal{P}_L$, this can be solved explicitly. Thus, one can show that

$$\begin{aligned} \mathcal{Q}_L \tilde{G}_2^{(2)}(T_p, \tau') &= e_{(+)}^{-i} \int_0^{T_p} ds \mathcal{Q}_L \tilde{L}_{eb}(s) \mathcal{Q}_L \tilde{G}_2^{(2)}(0, \tau') \\ &- i \int_0^{T_p} ds e_{(+)}^{-i} \int_0^s ds' \mathcal{Q}_L \tilde{L}_{eb}(s') \mathcal{Q}_L \tilde{L}_{eb}(s) \rho_b \tilde{g}_2^{(2)}(s, \tau') \end{aligned} \quad (B16)$$

$$\begin{aligned} \frac{d}{dT_p} \tilde{g}_2^{(2)}(T_p, \tau') &= \\ &- i \text{Tr}_b \left\{ \tilde{L}_{eb}(T_p) e_{(+)}^{-i} \int_0^{T_p} ds \mathcal{Q}_L \tilde{L}_{eb}(s) \mathcal{Q}_L \tilde{G}_2^{(2)}(0, \tau') \right\} \\ &- \int_0^{T_p} ds \text{Tr}_b \left\{ \tilde{L}_{eb}(T_p) e_{(+)}^{-i} \int_0^s ds' \mathcal{Q}_L \tilde{L}_{eb}(s') \mathcal{Q}_L \tilde{L}_{eb}(s) \rho_b \right\} \\ &\times \tilde{g}_2^{(2)}(s, \tau'), \end{aligned} \quad (B17)$$

where $\mathcal{Q}_L \tilde{G}_2^{(2)}(0, \tau') = G_1(\tau') \mathcal{Q}_R$ and $\tilde{g}_2^{(2)}(0, \tau') = g_1^{(1)}(\tau')$. The equations governing the time evolution of $G_1(\tau') \mathcal{Q}_R$ and $g_1(\tau')$ are the same as Eqs. (B8) and (B9), except for the different initial condition, $G_1(0) = \rho_b |D_1\rangle \langle D_2|$. The resulting equations are as follows:

$$\begin{aligned} \mathcal{Q}_L \tilde{G}_1(\tau') &= -\frac{i}{\hbar} \int_0^\tau ds e_{(+)}^{-i} \int_0^s ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \\ &\times \mathcal{Q}_L \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(2)}(s) \end{aligned} \quad (B18)$$

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_1^{(2)}(\tau') &= -\frac{1}{\hbar^2} \int_0^\tau ds \text{Tr}_b\{\rho_b \tilde{H}_{eb}(\tau')\} \\ &\times e_{(+)}^{-i} \int_s^\tau ds' \mathcal{Q}_L \tilde{H}_{eb}(s') \mathcal{Q}_L \tilde{H}_{eb}(s) \tilde{g}_1^{(2)}(s) \end{aligned} \quad (B19)$$

Using Eqs. (B28) and (B16), and the following identities:

$$\begin{aligned}
 G_2^{(2)}(T_p, \tau) Q_R &= Q_L G_2^{(2)}(T_p, \tau) \\
 &= Q_L e^{-iL_b T_p} e^{-iL_e T_p} \tilde{G}_2^{(2)}(T_p, \tau) \\
 &= e^{-iL_b T_p} e^{-iL_e T_p} Q_L \tilde{G}_2^{(2)}(T_p, \tau)
 \end{aligned} \tag{B20}$$

$$\begin{aligned}
 Q_L \tilde{G}^{(2)}(0, \tau) &= Q_L \tilde{G}_1^{(2)}(\tau) \\
 &= Q_L e^{-iL_b \tau} e^{ih_e \tau / \hbar} \tilde{G}_1^{(2)}(\tau) \\
 &= e^{-iL_b \tau} e^{-ih_e \tau / \hbar} Q_L \tilde{G}_1^{(2)}(\tau),
 \end{aligned} \tag{B21}$$

the inhomogeneous term in Eq. (B13) can be expressed as

$$\begin{aligned}
 \tilde{I}_3^{(2)}(\tau, T_p, \tau) &\equiv \frac{i}{\hbar} Tr_b \left\{ \tilde{G}_2^{(3)}(0, T_p, \tau) Q_R e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\} \\
 &= \frac{i}{\hbar} Tr_b \left\{ \left(e^{-iL_b T_p} e^{-iL_e T_p} e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} e^{-iL_b \tau} \right. \right. \\
 &\quad \left. \left. \times e^{-ih_e \tau / \hbar} Q_L \tilde{G}_1^{(2)}(\tau) \right) e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\} \\
 &\quad + \frac{1}{\hbar} \int_0^{T_p} Tr_b ds \left\{ \left(e^{-iL_b T_p} e^{-iL_e T_p} e_{(+)}^{-i \int_0^{T_p} ds' Q_L \tilde{L}_{eb}(s')} \right. \right. \\
 &\quad \left. \left. \times Q_L \tilde{L}_{eb}(s) \tilde{g}_2^{(2)}(s, \tau) \rho_b \right) e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\}
 \end{aligned} \tag{B22}$$

Inserting Eq. (B18) into the first of the above equation, we obtain the following final expression:

$$\begin{aligned}
 \tilde{I}_3^{(2)}(\tau, T_p, \tau) &= \frac{1}{\hbar^2} \int_0^\tau ds Tr_b \left\{ \left(e^{-iL_b T_p} e^{-iL_e T_p} e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} \right. \right. \\
 &\quad \left. \left. \times e^{-iL_b \tau} e^{-ih_e \tau / \hbar} e_{(+)}^{-\frac{i}{\hbar} \int_0^\tau ds' Q_L \tilde{H}_{eb}(s')} \right) \right. \\
 &\quad \left. \times Q_L \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(2)}(s) \times e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\} \\
 &\quad + \frac{1}{\hbar} \int_0^{T_p} ds Tr_b \left\{ \left(e^{-iL_b T_p} e^{-iL_e T_p} e_{(+)}^{-i \int_0^{T_p} ds' Q_L \tilde{L}_{eb}(s')} \right. \right. \\
 &\quad \left. \left. \times Q_L \tilde{L}_{eb}(s) \tilde{g}_2^{(2)}(s, \tau) \rho_b \right) e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\}
 \end{aligned} \tag{B23}$$

Similarly, the inhomogeneous term of Eq. (B17) can be shown to be

$$\begin{aligned}
 \tilde{I}_2^{(2)}(T_p, \tau) &\equiv -i Tr_b \left\{ \tilde{L}_{eb}(T_p) e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} Q_L \tilde{G}_2(0, \tau) \right\} \\
 &= -\frac{1}{\hbar} \int_0^\tau ds Tr_b \left\{ \tilde{L}_{eb}(T_p) e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} e^{-iL_e \tau} \right. \\
 &\quad \left. \times e^{-ih_e \tau / \hbar} e_{(+)}^{-\frac{i}{\hbar} \int_0^\tau ds' Q_L \tilde{H}_{eb}(s')} Q_L \tilde{H}_{eb}(s) \rho_b \tilde{g}_1^{(2)}(s) \right\}
 \end{aligned} \tag{B24}$$

3. Equations for $\chi^{(3)}(\tau, T_p, \tau')$. Define

$$\tilde{G}_3^{(3)}(\tau, T_p, \tau') = e^{iL_b \tau} G_3^{(3)}(\tau, T_p, \tau') e^{-ih_e \tau / \hbar}. \tag{B25}$$

Then, $\tilde{g}_3^{(3)}(\tau, T_p, \tau') = Tr_b \{ G_3^{(3)}(\tau, T_p, \tau') \}$. The equation governing the time evolution of $\tilde{g}_3^{(3)}(\tau, T_p, \tau')$ is the same as $\tilde{g}_2^{(2)}(\tau, T_p, \tau')$ except for the difference in the initial condition. Thus,

$$\begin{aligned}
 \frac{d}{d\tau} \tilde{g}_3^{(3)}(\tau, T_p, \tau') &= \frac{i}{\hbar} Tr_b \left\{ \tilde{G}_3^{(3)}(0, T_p, \tau') Q_R e_{(-)}^{\frac{i}{\hbar} \int_0^\tau ds \tilde{H}_{eb}(s) Q_R} \tilde{H}_{eb}(\tau) \right\} \\
 &\quad - \int_0^\tau ds \tilde{g}_3^{(3)}(s, T_p, \tau') \\
 &\quad \times Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) Q_R e_{(-)}^{\frac{i}{\hbar} \int_s^\tau ds' \tilde{H}_{eb}(s') Q_R} \tilde{H}_{eb}(\tau) \right\},
 \end{aligned} \tag{B26}$$

where

$$\begin{aligned}
 \tilde{g}_3^{(3)}(0, T_p, \tau') &= |D_4\rangle \langle D_3| Tr_b \{ G_2^{(3)}(T_p, \tau') \} \\
 &= |D_4\rangle \langle D_3| g_2^{(3)}(T_p, \tau')
 \end{aligned} \tag{B27}$$

$$\tilde{G}_3^{(3)}(0, T_p, \tau') Q_R = |D_4\rangle \langle D_3| G_2^{(3)}(T_p, \tau') Q_R \tag{B28}$$

The time evolution equations for $\tilde{g}_2^{(3)}(T_p, \tau')$ are the same as $\tilde{g}_2^{(2)}(T_p, \tau')$. Thus, one can show that

$$\begin{aligned}
 Q_L \tilde{G}_2^{(3)}(T_p, \tau') &= e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} Q_L \tilde{G}_2^{(3)}(0, \tau') \\
 &\quad - i \int_0^{T_p} ds e_{(+)}^{-i \int_s^{T_p} ds' Q_L \tilde{L}_{eb}(s')} Q_L \tilde{L}_{eb}(s) \rho_b \tilde{g}_2^{(3)}(s, \tau') \\
 \frac{d}{dT_p} \tilde{g}_2^{(3)}(T_p, \tau') &= -i Tr_b \left\{ \tilde{L}_{eb}(T_p) e_{(+)}^{-i \int_0^{T_p} ds Q_L \tilde{L}_{eb}(s)} Q_L \tilde{G}_2(0, \tau') \right\}
 \end{aligned} \tag{B29}$$

$$-\int_0^{\tau} ds Tr_b \left\{ \tilde{\mathcal{L}}_{eb}(T_p) e_{(+)}^{-i \int_0^{\tau} ds' \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s')} \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s) \rho_b \right\} \times \tilde{g}_2^{(3)}(s, \tau), \quad (B30)$$

where $\mathcal{Q}_L \tilde{G}_2^{(3)}(0, \tau) = G_1^{(3)}(\tau) \mathcal{Q}_R$ and $\tilde{g}_2^{(3)}(0, \tau) = g_1^{(3)}(\tau)$. The equations governing the time evolution of $G_1^{(3)}(\tau) \mathcal{Q}_R$ and $g_1^{(3)}(\tau)$ are as derived below.

Define a similar interaction picture for $\tilde{G}_1^{(3)}(\tau)$ such that

$$\tilde{G}_1^{(3)}(\tau) = e^{i\mathcal{L}_b \tau} G_1^{(3)}(\tau) e^{-ih_e \tau / \hbar}. \quad (B31)$$

Then, we obtain the following equations:

$$\begin{aligned} \tilde{G}_1^{(3)}(\tau) \mathcal{Q}_R &= \frac{i}{\hbar} \int_0^{\tau} ds \tilde{g}_1^{(3)}(s) \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{i \int_s^{\tau} ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \\ \frac{d}{d\tau} \tilde{g}_1^{(3)}(\tau) &= -\frac{1}{\hbar^2} \int_0^{\tau} ds \tilde{g}_1^{(3)}(s) Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R \right. \\ &\quad \left. \times e_{(-)}^{i \int_s^{\tau} ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\}. \end{aligned} \quad (B32)$$

The initial condition is such that $G_1^{(3)}(0) = \rho_b |D_2\rangle \langle D_1|$.

Using Eqs. (B28) and (B16), and the following identity

$$\begin{aligned} \mathcal{Q}_L \tilde{G}_2^{(3)}(0, \tau) &= \mathcal{Q}_L \tilde{G}_1^{(3)}(\tau) = \tilde{G}_1^{(3)}(\tau) \mathcal{Q}_R \\ &= e^{-i\mathcal{L}_b \tau} \tilde{G}_1^{(3)}(\tau) \mathcal{Q}_R e^{ih_e \tau / \hbar}, \end{aligned} \quad (B33)$$

the inhomogeneous term in Eq. (B13) can be expressed as

$$\begin{aligned} \tilde{I}_3^{(3)}(\tau, T_p, \tau') &\equiv \frac{i}{\hbar} Tr_b \left\{ \tilde{G}_3^{(2)}(0, T_p, \tau') \mathcal{Q}_R e_{(-)}^{i \int_0^{\tau} ds \tilde{H}_{eb}(s) \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\} \\ &= \frac{1}{\hbar^2} \int_0^{\tau} ds Tr_b \left\{ \left(e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} e_{(+)}^{-i \int_0^{T_p} ds \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s)} \right) \right. \\ &\quad \left. \times e^{-i\mathcal{L}_b \tau} e^{-ih_e \tau / \hbar} \tilde{g}_1^{(3)}(s) \tilde{H}_{eb}(s) \mathcal{Q}_R \right. \\ &\quad \left. \times e_{(-)}^{i \int_s^{\tau} ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \right\} e_{(-)}^{i \int_0^{\tau} ds \tilde{H}_{eb}(s) \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \\ &\quad + \frac{1}{\hbar} \int_0^{T_p} Tr_b ds \left\{ \left(e^{-i\mathcal{L}_b T_p} e^{-i\mathcal{L}_e T_p} e_{(+)}^{-i \int_s^{T_p} ds' \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s')} \right) \right. \\ &\quad \left. \times \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s) \tilde{g}_2^{(2)}(s, \tau') \rho_b \right\} e_{(-)}^{i \int_0^{\tau} ds \tilde{H}_{eb}(s) \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \end{aligned} \quad (B34)$$

Similarly, the inhomogeneous term of Eq. (B17) can be shown to be

$$\begin{aligned} \tilde{I}_2^{(3)}(T_p, \tau') &\equiv -i Tr_b \left\{ \tilde{\mathcal{L}}_{eb}(T_p) e_{(+)}^{-i \int_0^{T_p} ds \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s)} \mathcal{Q}_L \tilde{G}_2(0, \tau') \right\} \\ &= \frac{1}{\hbar} \int_0^{\tau} ds Tr_b \left\{ \tilde{\mathcal{L}}_{eb}(T_p) e_{(+)}^{-i \int_0^{T_p} ds \mathcal{Q}_L \tilde{\mathcal{L}}_{eb}(s)} e^{-i\mathcal{L}_e \tau} \right. \\ &\quad \left. \times e^{-ih_e \tau / \hbar} (\tilde{g}_1^{(3)}(s) \tilde{H}_{eb}(s) \mathcal{Q}_R \times e_{(-)}^{i \int_s^{\tau} ds' \tilde{H}_{eb}(s') \mathcal{Q}_R}) \right\} \end{aligned} \quad (B35)$$

Equations for $\chi^{(4)}(\tau, T_p, \tau')$. The equations for this can be derived in a similar manner as $\chi^{(1)}(\tau, T_p, \tau')$. First, define

$$\begin{aligned} \tilde{G}_3^{(4)}(\tau, T_p, \tau') &\equiv e^{iH_b \tau / \hbar} G_3^{(4)}(\tau, T_p, \tau') e^{-iH_b \tau / \hbar} e^{-ih_e \tau / \hbar} \\ &= e^{i\mathcal{L}_b \tau} G_3^{(4)}(\tau, T_p, \tau') e^{-ih_e \tau / \hbar}, \end{aligned} \quad (B36)$$

Then,

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_3^{(4)}(\tau, T_p, \tau') &= \frac{i}{\hbar} Tr_b \left\{ \tilde{G}_3^{(4)}(0, T_p, \tau') \mathcal{Q}_R e_{(-)}^{i \int_0^{\tau} ds \tilde{H}_{eb}(s) \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\} \\ &\quad - \int_0^{\tau} ds \tilde{g}_3^{(4)}(s, T_p, \tau') \\ &\quad \times Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{i \int_s^{\tau} ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\}, \end{aligned} \quad (B37)$$

where

$$\begin{aligned} \tilde{g}_3^{(4)}(0, T_p, \tau') &= Tr_b \{ G_1^{(4)}(\tau') \} |D_2\rangle \langle D_3| \\ &= g_1^{(4)}(\tau') |D_2\rangle \langle D_3|, \end{aligned} \quad (B38)$$

$$\begin{aligned} \tilde{G}_3^{(4)}(0, T_p, \tau') \mathcal{Q}_R &= (e^{-i\mathcal{L}_b T_p} G_1^{(4)}(\tau')) |D_2\rangle \langle D_3| \mathcal{Q}_R \\ &= e^{-i\mathcal{L}_e T_p} (G_1^{(4)}(\tau') \mathcal{Q}_R) |D_2\rangle \langle D_3|. \end{aligned} \quad (B39)$$

Thus, solution of Eq. (B4) requires information on $g_1^{(4)}(\tau')$, which can be obtained from $G_1^{(4)}(\tau') \mathcal{P}_R$, and that on $G_1^{(4)}(\tau') \mathcal{Q}_R$. The time evolutions for these can be obtained by employing a similar procedure. Defining a similar interaction picture for $\tilde{G}_1^{(4)}(\tau')$ such that

$$\tilde{G}_1^{(4)}(\tau') = e^{i\mathcal{L}_b \tau'} G_1^{(4)}(\tau') e^{-ih_e \tau' / \hbar}. \quad (B40)$$

Then, we obtain the following equations:

$$\begin{aligned} \tilde{G}_1^{(4)}(\tau) \mathcal{Q}_R &= \frac{i}{\hbar} \int_0^\tau ds \tilde{g}_1^{(4)}(s) \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{i \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \\ \frac{d}{d\tau} \tilde{g}_1^{(4)}(\tau) &= -\frac{1}{\hbar^2} \int_0^\tau ds \tilde{g}_1^{(4)}(s) Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R \right. \\ &\quad \left. \times e_{(-)}^{i \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\}. \end{aligned} \quad (\text{B41})$$

Combining Eqs. (B6), (B7), and (B8), we find that

$$\begin{aligned} \tilde{G}_3^{(4)}(0, T_p, \tau) \mathcal{Q}_R &= \frac{i}{\hbar} e^{-iL_b(T_p+\tau)} \int_0^\tau ds \tilde{g}_1^{(4)}(s) \tilde{H}_{eb}(s) \\ &\quad \times e_{(-)}^{i \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} e^{iH_e \tau / \hbar} |D_2\rangle \langle D_3|. \end{aligned} \quad (\text{B42})$$

Inserting this into Eq. (B37), we find that

$$\begin{aligned} \frac{d}{d\tau} \tilde{g}_3^{(4)}(\tau, T_p, \tau) &= -\frac{1}{\hbar^2} \int_0^\tau ds Tr_b \left\{ (\rho_b \tilde{g}_1^{(4)}(s) \tilde{H}_{eb}(s) \right. \\ &\quad \times e_{(-)}^{i \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} e^{iH_e \tau / \hbar} |D_2\rangle \langle D_3|) \\ &\quad \times e^{iL_b(T_p+\tau)} e_{(-)}^{i \int_0^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \left. \right\} \\ &\quad - \int_s^\tau ds \tilde{g}_3^{(1)}(s, T_p, \tau) \\ &\quad \times Tr_b \left\{ \rho_b \tilde{H}_{eb}(s) \mathcal{Q}_R e_{(-)}^{i \int_s^\tau ds' \tilde{H}_{eb}(s') \mathcal{Q}_R} \tilde{H}_{eb}(\tau) \right\}. \end{aligned} \quad (\text{B43})$$

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