

**THE BETHE-SALPETER-KADANOFF-BAYM  
APPROACH TO TIME- AND  
FREQUENCY-RESOLVED FLUORESCENCE  
IN MOLECULAR NANOSTRUCTURES**

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ABSTRACT

The time- and frequency-resolved fluorescence of molecular aggregates with strong exciton-phonon interaction (i.e., when the absorption linewidth of single molecule is larger than the intermolecular interactions) is calculated. The fluorescence signal is related to the molecular electronic population variables by means of an exact generalized Kadanoff-Baym Ansatz, whose parameters are calculated perturbatively.

**1. Introduction**

The optical response of molecular aggregates constitutes an important and complex theoretical problem. Electronic excitations in molecular aggregates are Frenkel excitons [1, 2], which are quasiparticles that can be scattered on each other due to their non-boson statistics (Pauli exclusion principle) and the Coulomb interactions. Exciton coherent motion is an evidence of aggregation, and exciton-exciton scattering is an important mechanism for optical nonlinearities. Interaction of excitons with a bath or nuclear motions including intermolecular, intramolecular, and solvent degrees of freedom brings incoherence into exciton motion which shows up in various optical measurements. Despite a relatively simple structure of electronic excitations in molecular aggregates, theoretical modeling of incoherent exciton motion constitutes a genuine many-body problem because of the macroscopically large number of solvent degrees of freedom. Even in the simplest case of a dimer of two-level molecules interacting with a harmonic heat bath (in the context of quantum dissipation this model is known as the spin-boson model), the problem does not have an exact solution [3] and may not be treated perturbatively in the case of strong coupling to the bath.

Since calculations of the time- and frequency-resolved fluorescence signal involve one-exciton states only [4,5] it is the simplest observable which illustrates the role of incoherent exciton motion in optical measurements. The role of incoherent exciton motion in coherent four wave mixing measurement was discussed in [6,7].

## II. Green Function Expressions for the Fluorescence Signal

We consider an aggregate made of two-level molecules with dipole-dipole interactions treated within the Heitler-London approximation. We assume that each molecule is coupled to its own Harmonic nuclear bath [5]. The Hamiltonian has a form

$$\begin{aligned}\hat{H} &= \hat{H}^{(0)} + \hat{H}_{int} \\ \hat{H}^{(0)} &\equiv \sum_m \hat{H}^{(m)}\end{aligned}\quad (2.1)$$

where  $\hat{H}^{(m)}$  is the Hamiltonian of the  $m$ th molecule coupled to its bath and  $\hat{H}_{int}$  is the intermolecular coupling [5,14,18]

$$\begin{aligned}\hat{H}^{(m)} &\equiv \Omega_m \hat{B}_m^+ \hat{B}_m + \sum_{\alpha} \omega_{m\alpha} \hat{c}_{m\alpha}^+ \hat{c}_{m\alpha} \\ &+ \frac{1}{\sqrt{2}} \sum_{\alpha} \omega_{m\alpha} d_{m\alpha} (\hat{c}_{m\alpha}^+ + \hat{c}_{m\alpha}) \hat{B}_m^+ \hat{B}_m,\end{aligned}\quad (2.2)$$

$$\hat{H}_{int} = \sum_{mn} J_{mn} \hat{B}_m^+ \hat{B}_n. \quad (2.3)$$

$\hat{B}_m^+$  ( $\hat{B}_m$ ) are the exciton annihilation (creation) operators which satisfy the commutation relations

$$[\hat{B}_m, \hat{B}_n^+] = \delta_{mn} (1 - 2\hat{B}_m^+ \hat{B}_m). \quad (2.4)$$

$\hat{c}_{m\alpha}$  and  $\hat{c}_{m\alpha}^+$  are the bath variables of the  $m$ 'th molecule.  $\Omega_m$  is the transition frequency of the  $m$ 'th molecule,  $\omega_{m\alpha}$  and  $d_{m\alpha}$  are the frequencies and the dimensionless displacements of the bath oscillators,  $J_{mn}$  represent intermolecular interactions. The Hamiltonian of the system driven by the external field  $\epsilon(\tau)$  has the form

$$\hat{H}(\tau) = \hat{H} - \sum_n \epsilon_n(\tau) (\hat{B}_n^+ + \hat{B}_n), \quad (2.5)$$

with

$$\epsilon_n(\tau) \equiv \mu_n \epsilon(\tau), \quad (2.6)$$

we have assumed that the aggregate size is much smaller than the optical wavelength.

We now introduce three types of exciton operators in the interaction representations  $\bar{B}_m(\tau)$ ,  $\tilde{B}_m(\tau)$ , and  $\hat{B}_m(\tau)$ , corresponding to time evolution with

the Hamiltonians  $\hat{H}^{(0)}$ ,  $\hat{H}$ , and  $\hat{H}$ , respectively. The time- and frequency-resolved fluorescence spectrum  $I(\Omega, \tau)$  can be expressed in terms of the two-time nonequilibrium Green function in the system driven by the external field [4-6] (we adopt the rotating-wave approximation)

$$\bar{C}_{mn}(t, t') \equiv \langle \tilde{B}_n^+(t') \tilde{B}_m(t) \rangle. \quad (2.7)$$

We then have

$$I(\Omega, \tau) \propto \sum_{mn} \mu_m \mu_n \int_{-\infty}^{+\infty} dt \bar{C}_{mn} \left( \tau + \frac{t}{2}, \tau - \frac{t}{2} \right) e^{i\Omega t} \quad (2.8)$$

To linear order in the exciting field intensity, i.e., to second order in its amplitude, the correlation function  $\bar{C}_{mn}(t, t')$  can be expressed in terms of a four-time correlation function of exciton operators in the free system (without the external field) [5,6]:

$$\bar{C}_{mn}(t, t') = \sum_{pq} \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' \bar{C}_{mn,pq}(t, t'; \tau, \tau') \epsilon_p(\tau) \epsilon_q^*(\tau') \quad (2.9)$$

with

$$\bar{C}_{mn,pq}(t, t', \tau, \tau') \equiv \langle \tilde{B}_q(\tau') \tilde{B}_n^+(t') \tilde{B}_m(t) \tilde{B}_p^+(\tau) \rangle \quad (2.10)$$

The Green function expressions for the signal [Eqs. (2.9) and (2.10)] is our starting point for calculations of the time- and frequency-resolved fluorescence. In the following sections we explore several methods for evaluating the Green function in Eq. (2.10) representing the signal [see Eqs. (2.7) - (2.9)].

### III. The Bethe-Salpeter Equation

The most direct way to calculate Eq. (2.7) is by solving an equation of evolution for the signal itself. An equation of motion for a two-time nonequilibrium Green function is known as the Bethe-Salpeter equation [22]. In our case it adopts a form:

$$\begin{aligned}\bar{C}_{mn}(t, t') &= \bar{C}_{mn}(t, t') \\ &+ \sum_{kl} \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' M_{mn,kl}(t, t'; \tau, \tau') \bar{C}_{kl}(\tau, \tau')\end{aligned}\quad (3.1)$$

where  $\bar{C}_{mn}(t, t')$ , the correlation function  $\bar{C}_{mn}(t, t')$  in an aggregate with no intermolecular interactions  $J_{mn} = 0$ , can be evaluated exactly. The kernel

$$\begin{aligned}
& + \theta(t-t') \sum_{kl} \int_{-\infty}^{t'} d\tau' \int_{\tau'}^t d\tau C_{mn,kl}(t, t'; \tau, \tau') \epsilon_k(\tau) \epsilon_l^*(\tau') \\
& + \theta(t'-t) \sum_{kl} \int_{-\infty}^{t'} d\tau' \int_{\tau'}^t d\tau C_{mn,kl}(t, t'; \tau, \tau') \epsilon_k(\tau) \epsilon_l^*(\tau') \\
& + \theta(t'-t) \sum_{kl} \int_{-\infty}^{t'} d\tau' \int_{\tau'}^t d\tau C_{mn,kl}(t, t'; \tau, \tau') \epsilon_k(\tau) \epsilon_l^*(\tau')
\end{aligned} \quad (4.3)$$

Each of the six pathways contains three evolution periods, during the first and the third intervals the density matrix is in the ground-excited states coherence ( $\hat{\rho}_{0n}$  or  $\hat{\rho}_{n0}$ ). During the second time interval the density matrix is represented by either a ground state wavepacket  $\hat{\rho}_{00}$  (Raman) or by excited state wavepackets  $\hat{\rho}_{mn}$  (fluorescence).

The equations of motion for the wavepackets are

$$\frac{d\hat{\rho}_{00}(\tau)}{d\tau} + i\mathcal{L}_{00,00}\hat{\rho}_{00}(\tau) = 0, \quad (4.4)$$

$$\frac{d\hat{\rho}_{n0}(\tau)}{d\tau} + i \sum_n \mathcal{L}_{m0,n0}\hat{\rho}_{n0}(\tau) = 0, \quad (4.5)$$

$$\frac{d\hat{\rho}_{0n}(\tau)}{d\tau} + i \sum_n \mathcal{L}_{0n,0n}\hat{\rho}_{0n}(\tau) = 0, \quad (4.6)$$

$$\frac{d\hat{\rho}_{mn}(\tau)}{d\tau} + i \sum_{pq} \mathcal{L}_{mn,pq}\hat{\rho}_{pq}(\tau) = 0. \quad (4.7)$$

The Liouville operators in Eqs. (4.4) - (4.7) are given by

$$\mathcal{L} = L + \bar{J}, \quad (4.8)$$

with

$$\begin{aligned}
L_{00,00}\hat{\xi} &= [\bar{H}_0, \hat{\xi}], \\
L_{m0,n0}\hat{\xi} &= \delta_{mn}(\bar{H}_m\hat{\xi} - \hat{\xi}\bar{H}_0), \\
L_{0n,0n}\hat{\xi} &= \delta_{nn}(\bar{H}_0\hat{\xi} - \hat{\xi}\bar{H}_n), \\
L_{mn,pq}\hat{\xi} &= \delta_{mp}\delta_{nq}(\bar{H}_m\hat{\xi} - \hat{\xi}\bar{H}_n)
\end{aligned} \quad (4.9)$$

and

$$\begin{aligned}
\bar{J}_{00,00} &\equiv 0, \quad \bar{J}_{m0,n0}\hat{\xi} = J_{mn}\hat{\xi}, \quad \bar{J}_{0n,0n}\hat{\xi} = -J_{nn}\hat{\xi} \\
\bar{J}_{mn,pq}\hat{\xi} &= (J_{mp}\delta_{nq} - \delta_{mp}J_{nq})\hat{\xi}.
\end{aligned} \quad (4.10)$$

The Hamiltonians  $\bar{H}_0$  and  $\bar{H}_m$  are defined as

$$\begin{aligned}
\bar{H}_0 &\equiv \sum_{na} \omega_{na} \hat{c}_{na}^+ \hat{c}_{na}, \\
\bar{H}_m &\equiv \sum_{na} \omega_{na} \hat{c}_{na}^+ \hat{c}_{na} + \Omega_m + \frac{1}{\sqrt{2}} \sum_{\alpha} \omega_{m\alpha} d_{m\alpha} (\hat{c}_{m\alpha}^+ + \hat{c}_{m\alpha}),
\end{aligned} \quad (4.11)$$

and  $\hat{\xi}$  is an arbitrary density operator in the phase space of nuclei.

The signal  $\bar{C}$  can be written using the Green functions of the Liouville equation  $\mathcal{G}$  [5] which in our notation represent the electronic matrix elements of the operator  $\exp(-i\mathcal{L}\tau)$ . The Green functions  $\mathcal{G}(\tau)$  are thus defined through the formal solution of Eqs. (4.4) - (4.7)

$$\hat{\rho}_{00}(\tau) = \mathcal{G}_{00,00}(\tau - \tau') \hat{\rho}_{00}(\tau') \quad (4.12)$$

$$\hat{\rho}_{n0}(\tau) = \sum_n \mathcal{G}_{m0,n0}(\tau - \tau') \hat{\rho}_{n0}(\tau') \quad (4.13)$$

$$\hat{\rho}_{0n}(\tau) = \sum_n \mathcal{G}_{0n,0n}(\tau - \tau') \hat{\rho}_{0n}(\tau') \quad (4.14)$$

$$\hat{\rho}_{mn}(\tau) = \sum_{pq} \mathcal{G}_{mn,pq}(\tau - \tau') \hat{\rho}_{pq}(\tau') \quad (4.15)$$

The signal can be written in the form of Eq. (4.1) with

$$\begin{aligned}
\bar{C}_{mn}^{(R)}(t, t') &= \theta(t-t') \sum_{kl} \int_{t'}^t d\tau' \int_{-\infty}^{\tau'} d\tau \\
& \langle \mathcal{G}_{m0,k0}(t-\tau) \mathcal{G}_{00,00}(\tau-t') \mathcal{G}_{0n,0l}(t'-\tau') \hat{\rho}_{gl} \epsilon_k(\tau) \epsilon_l^*(\tau') \rangle \\
& + \theta(t'-t) \sum_{kl} \int_{t'}^t d\tau' \int_{-\infty}^{\tau'} d\tau \\
& \langle \mathcal{G}_{0n,0l}(t'-\tau') \mathcal{G}_{00,00}(\tau-t) \mathcal{G}_{m0,k0}(t-\tau) \hat{\rho}_{gl} \epsilon_k(\tau) \epsilon_l^*(\tau') \rangle
\end{aligned} \quad (4.16)$$

and

$$\begin{aligned}
\bar{C}_{mn}^{(F)}(t, t') &= \theta(t-t') \sum_{klpq} \int_{\tau'}^t d\tau' \int_{-\infty}^{\tau'} d\tau \\
& \langle \mathcal{G}_{m0,p0}(t-t') \mathcal{G}_{qn,ql}(t'-\tau') \mathcal{G}_{p0,k0}(\tau'-\tau) \hat{\rho}_{gl} \epsilon_k(\tau) \epsilon_l^*(\tau') \rangle \\
& + \theta(t-t') \sum_{klpq} \int_{\tau'}^t d\tau' \int_{-\infty}^{\tau'} d\tau
\end{aligned}$$

$$C_{mn}(t, t') = C_{mn}^{(s)}(t, t') + \sum_k \int dt g_{mn,k}(t, t'; \tau) \rho_k(\tau), \quad (5.11)$$

where

$$\rho_k(\tau) \equiv C_{kk}(\tau, \tau), \quad (5.12)$$

is the electronic population of the  $k$ th molecule.

The function  $C_{mn}^{(s)}(t, t')$  is the short-time component of the signal,  $g_{mn,k}(t, t'; \tau)$  is the window function which expresses the long-time component of the signal in terms of the time-dependent molecular populations. The latter satisfy the inhomogeneous master equation

$$\frac{d\rho_m(\tau)}{d\tau} = \sum_n \int_{-\infty}^{\tau} d\tau' K_{mn}(\tau - \tau') \rho_n(\tau') + f_m(\tau) \quad (5.13)$$

where  $K_{mn}(\tau)$  is the memory kernel, and the source  $f_m(\tau)$

$$f_m(\tau) = \sum_{kl} \int d\tau' d\tau'' f_{m,kl}(\tau; \tau', \tau'') \epsilon_k(\tau') \epsilon_l^*(\tau'') \quad (5.14)$$

is the doorway function which describes the creation of the populations due to the external field. Eq. (5.13) has a form of a master equation. Eqs. (5.11) and (5.13) together with Eq. (5.14) provide a closed system of equations for calculating the time- and frequency-resolved fluorescence signal.

The memory function  $K_{mn}(\tau)$  the short-time component of the signal  $C_{mn}^{(s)}(t, t')$ , the door function  $f_m(\tau)$  and the window-function  $g_{mn,k}(t, t'; \tau)$  have the form:

$$K_{mn}(\tau) = - \sum_{pqrs} \text{Tr}[\bar{J}_{mn,pq} \mathcal{G}_{pq,rs}(\tau) \bar{J}_{rs,mn} \hat{\rho}^{(n)}] \quad (5.15)$$

$$f_n(\tau) = -i \sum_m \int_{-\infty}^{\tau} d\tau' \text{Tr}[\mathcal{G}_{nm}^+(\tau - \tau') \hat{\rho}_n \epsilon_n(\tau) \epsilon_m^*(\tau')]$$

$$-i \sum_m \int_{-\infty}^{\tau} d\tau' \text{Tr}[\mathcal{G}_{nm}^-(\tau - \tau') \hat{\rho}_n \epsilon_n^*(\tau) \epsilon_m(\tau')]$$

$$+i \sum_{pqrsk} \int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau'} d\tau''$$

$$\text{Tr}[\bar{J}_{nn,pq} \mathcal{G}_{pq,rs}(\tau - \tau') Q \mathcal{G}_{sk}^+(\tau' - \tau'') \hat{\rho}_n \epsilon_n(\tau') \epsilon_k^*(\tau'')]$$

$$+i \sum_{pqrsk} \int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau'} d\tau''$$

$$\text{Tr}[\bar{J}_{nn,pq} \mathcal{G}_{pq,rs}(\tau - \tau') Q \mathcal{G}_{sk}^-(\tau' - \tau'') \hat{\rho}_n \epsilon_n^*(\tau') \epsilon_k(\tau'')] \quad (5.16)$$

$$g_{mn,k}(t, t'; \tau) = \theta(t - t') \delta(t' - \tau) \delta_{nk} \text{Tr}[\mathcal{G}_{mn}^-(t - t') \hat{\rho}^{(n)}] \\ + \theta(t' - t) \delta(t - \tau) \delta_{nk} \text{Tr}[\mathcal{G}_{mn}^+(t' - t) \hat{\rho}^{(m)}] \\ - i\theta(t - t') \sum_{pqrs} \text{Tr}[\mathcal{G}_{mp}^-(t - t') \mathcal{G}_{pq,rs}(t' - \tau) \bar{J}_{rs,kk} \hat{\rho}^{(k)}] \\ - i\theta(t' - t) \sum_{pqrs} \text{Tr}[\mathcal{G}_{mp}^+(t' - t) \mathcal{G}_{pq,rs}(t - \tau) \bar{J}_{rs,kk} \hat{\rho}^{(k)}] \quad (5.17)$$

$$C_{mn}^{(s)}(t, t') = \theta(t - t') \int_{-\infty}^{t'} d\tau' \int_{t'}^{\tau} d\tau \\ \text{Tr}[\mathcal{G}_{mp}^-(t - \tau) \mathcal{G}^{(0)}(\tau - t') \mathcal{G}_{nq}^+(t' - \tau') \hat{\rho}_q] \epsilon_p(\tau) \epsilon_q^*(\tau') \\ + \theta(t' - t) \int_{-\infty}^{t'} d\tau' \int_{t'}^{\tau} d\tau'' \\ \text{Tr}[\mathcal{G}_{nq}^+(t' - \tau') \mathcal{G}^{(0)}(\tau' - t) \mathcal{G}_{mp}^-(t - \tau) \hat{\rho}_q] \epsilon_p(\tau) \epsilon_q^*(\tau') \\ + \theta(t - t') \sum_{rs} \int_{-\infty}^{t'} d\tau' \int_{-\infty}^{\tau} d\tau \\ \text{Tr}[\mathcal{G}_{ms}^-(t - t') \mathcal{G}_{sn,rq}(t' - \tau') Q \mathcal{G}_{rp}^-(\tau' - \tau) \hat{\rho}_q] \epsilon_p(\tau) \epsilon_q^*(\tau') \\ + \theta(t' - t) \sum_{rs} \int_{-\infty}^{t'} d\tau' \int_{-\infty}^{\tau} d\tau'' \\ \text{Tr}[\mathcal{G}_{ms}^+(t' - t) \mathcal{G}_{sn,rq}(t' - \tau) Q \mathcal{G}_{rp}^+(\tau - \tau') \hat{\rho}_q] \epsilon_p(\tau) \epsilon_q^*(\tau') \\ + \theta(t' - t) \sum_{rs} \int_{-\infty}^{t'} d\tau' \int_{-\infty}^{\tau'} d\tau \\ \text{Tr}[\mathcal{G}_{ns}^+(t' - t) \mathcal{G}_{ms,rq}(t - \tau') Q \mathcal{G}_{rp}^-(\tau' - \tau) \hat{\rho}_q] \epsilon_p(\tau) \epsilon_q^*(\tau') \quad (5.18)$$

The auxiliary functions in Eqs. (5.15) - (5.18) can be calculated perturbatively in  $J$ . The procedure is outlined in Appendix B. The memory function to second order in  $J$  is

$$K_{mn}(\tau) = \theta(\tau) |J_{mn}|^2 \int \frac{d\omega_1 d\omega_2}{(2\pi)^3} e^{-i\omega\tau} \\ \times \sigma_m(\omega_1) \sigma_n(\omega_2) \frac{2\omega}{\omega^2 - (\omega_1 - \omega_2)^2} \quad \text{for } m \neq n \quad (5.19)$$

$$K_{mn}(\tau) = \theta(\tau) \sum_{n \neq m} \int \frac{d\omega_1 d\omega_2}{(2\pi)^3} e^{-i\omega\tau} \\ \times \sigma_n(\omega_1) \sigma_m(\omega_2) \frac{2\omega}{\omega^2 - (\omega_1 - \omega_2)^2} \quad (5.20)$$

an expectation value in the ground state using Eq. (B10). The correlation functions in Eqs. (A1) through (A6) can be expressed in terms of functions  $g_m(\tau)$  [5] defined as

$$g_m(\tau) \equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{c_m(\omega)}{\omega^2} \{ [1 - \cos(\omega\tau)] \coth\left(\frac{\omega}{2T}\right) - i \sin(\omega\tau) - \omega\tau \} \quad (\text{A7})$$

with

$$c_m(\omega) \equiv \frac{1}{2} \sum_{\alpha} \omega_{m\alpha} d_{m\alpha}^2 [\delta(\omega - \omega_{m\alpha}) - \delta(\omega + \omega_{m\alpha})] \quad (\text{A8})$$

The functions  $g_m(\tau)$  contain all the relevant information about the bath properties and the signals can be expressed in terms of  $\Omega_m$ ,  $J_m$ , and  $g_m(\tau)$ .

To present expressions for single-molecule correlation functions in the most general form we introduce correlation functions of the  $2N$ th order ( $N = 1, 2, \dots$ )  $\Gamma_m^{(N)}$  and  $\bar{\Gamma}_m^{(N)}$  in the following way

$$\Gamma_m^{(N)}(t_1, t'_1; \dots; t_N, t'_N) \equiv (\bar{B}_m(t_1) \bar{B}_m^+(t'_1) \dots \bar{B}_m(t_N) \bar{B}_m^+(t'_N)) \quad (\text{A9})$$

$$\begin{aligned} & \Gamma_m^{(N)}(t_1, t'_1; \dots; t_N, t'_N) \\ & \equiv \lim_{\tau_0 \rightarrow -\infty} (\bar{B}_m(\tau_0) \bar{B}_m^+(t_1) B_m(t'_1) \dots \bar{B}_m^+(t_N) B_m(t'_N) \bar{B}_m^+(\tau_0)) \end{aligned} \quad (\text{A10})$$

In particular, we have  $\sigma_m = \Gamma_m^{(1)}$ ,  $\Gamma_m = \Gamma_m^{(2)}$ ,  $\bar{\Gamma}_m = \Gamma_m^{(3)}$ ,  $\sigma'_m = \Gamma_m^{(1)}$ ,  $\Gamma_m^{\nu} = \Gamma_m^{(2)}$ ,  $\bar{\Gamma}_m^{\nu} = \Gamma_m^{(3)}$ .

The correlation function in Eq. (A9) can be evaluated using various methods, e.g., decomposition through coherent states of oscillators or applying canonical transformations. Expressions for  $\Gamma_m^{(N)}$  in the case  $N = 1$  and  $N = 2$  are given in [5]. Straightforward calculations yield

$$\begin{aligned} & \Gamma_m^{(N)}(t_1, t'_1; \dots; t_N, t'_N) \\ & = \exp \left[ -i\Omega_m \sum_{j=1}^N (t_j - t'_j) - F_m^{(N)}(t_1, \dots, t_N; t'_1, \dots, t'_N) \right] \end{aligned} \quad (\text{A11})$$

where

$$\begin{aligned} & F_m^{(N)}(t_1, \dots, t_N; t'_1, \dots, t'_N) = \sum_{i=1}^N g_m(t_i - t'_i) \\ & + \sum_{j=1}^{N-1} \sum_{i=1}^{j-1} [g_m(t_i - t'_j) + g_m(t'_j - t_j) - g_m(t_i - t_j) - g_m(t'_i - t'_j)] \end{aligned} \quad (\text{A12})$$

The function  $F_m^{(N)}$  can be written using the following rules. One needs to make a sum of contributions related to pairs of operators in the r.h.s. of Eq.

(A9). Each contribution is a  $g_m$  function of the difference of times in these operators and it should be written in a form  $g_m(\tau' - \tau'')$  if the operator at time  $\tau'$  stands to the left of the operator at time  $\tau''$ . In addition, the contribution comes with the sign "minus" if both operators are  $\bar{B}$  or  $\bar{B}^+$  and with the sign "plus" if one of them is  $\bar{B}$  and the other is  $\bar{B}^+$ .

The functions  $\Gamma_m^{(N)}$  can be obtained by combining Eq. (A10) with Eqs. (A11) and (A12), and making use of the asymptotic behavior of the functions  $g_m(\tau)$  at large time  $\tau$ :

$$g_m(\tau) = \delta_n |\tau| - i\lambda_n \tau + \bar{g}_m(\tau) \quad (\text{A13})$$

where  $\bar{g}_m(\tau)$  has finite limits at  $\tau \rightarrow \pm\infty$ , the constant  $\delta_n$  will not enter expressions for  $\bar{\Gamma}_m^{(N)}$  and  $\lambda_m$  can be expressed in terms of  $c_m(\omega)$ :

$$\lambda_m = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{c_m(\omega)}{\omega} \quad (\text{A14})$$

$\Gamma_m^{(N)}$  are given by

$$\begin{aligned} & \Gamma_m^{(N)}(t_1, \dots, t_N; t'_1, \dots, t'_N) \\ & = \exp[-i(\Omega_m - 2\lambda_m) \sum_{j=1}^N (t'_j - t_j) - F_m^{(N)}(t_1, \dots, t_N; t'_1, \dots, t'_N)] \end{aligned} \quad (\text{A15})$$

## APPENDIX B: Perturbation Theory for the GKBA and the Master Equations

In Section V we have derived an equation of motion for the populations and the GKBA for the signal. The ingredients of these expressions  $f_m$ ,  $g_{mn,k}$ ,  $K_{mn}$ , and  $C_{mn}^{(j)}$  are expressed in terms of the Green functions of the Liouville equation  $\mathcal{G}^{(\pm)}$ ,  $\mathcal{G}^{(0)}$ , and  $\mathcal{G}$ , the projector operator  $Q$ , and the density operators  $\hat{\rho}_g$  and  $\hat{\rho}^{(m)}$  [Eqs. (5.15) through (5.18)]. In this appendix we show how to evaluate the traces in Eqs. (5.15) through (5.18) perturbatively in  $J$ . Each perturbative term can be expressed in terms of multitime correlation functions of  $\bar{B}(\tau)$  and  $\bar{B}^+(\tau)$  operators in single molecules which can be evaluated exactly. This provides a regular perturbative procedure of calculating the parameters of the basic equations of the theory. To calculate the traces in Eqs. (5.15) through (5.18), we note that the operators  $\mathcal{G}_{mn}^{(\pm)}(\tau)$  are the Green functions of the Liouville operators, i.e., the operator  $\exp(-i\mathcal{L}\tau)$  acting in the subspace of ground state-excited states coherence wavepackets and written in the matrix form with respect to electronic variables.  $\mathcal{G}^{(0)}(\tau)$  is the same operator acting in

## APPENDIX C: The Window Function

In this appendix we obtain the window function  $g_{mn,k}(t, t'; \tau)$ , introduced in Section V, perturbatively to the second order in  $J$ :

$$g = g^{(0)} + g^{(1)} + g^{(2)} \quad (C1)$$

To that end we make use of Eq. (5.17) expressing the window function in terms of the Green functions of the Liouville equation ( $G^{(\pm)}$  and  $G$ ) and apply the perturbative procedure of calculating the traces described in Appendix A. This yields:

$$g_{mn,m}^{(0)}(t, t'; \tau) = [(\theta(t-t')\delta(t'-\tau) + \theta(t'-t)\delta(t-\tau))] \times \sigma'_m(t'-t) \quad (C2)$$

$$g_{mn,m}^{(1)}(t, t'; \tau) = iJ_{mn}\theta(t-\tau)\theta(t'-\tau)\sigma'_m(\tau-t)\sigma_n(\tau-t') + iJ_{mn}\theta(t'-t)\delta(t-\tau) \int_t^{t'} dt' \sigma'_m(\tau'-t)\sigma_n(\tau'-t') \quad (C3)$$

$$g_{mn,m}^{(1)}(t, t'; \tau) = -iJ_{mn}\theta(t-\tau)\theta(t'-\tau)\sigma'_m(t'-\tau)\sigma_n(t-\tau) - iJ_{mn}\theta(t-t')\delta(t'-\tau) \int_t^{t'} dt' \sigma'_m(t'-\tau')\sigma_n(t-\tau') \quad (C4)$$

$$g_{mk,n}^{(2)}(t, t'; \tau) = J_{mn}J_{nk}\theta(t-\tau)\theta(t'-\tau) \times \left\{ \theta(t-\tau)\sigma_k(\tau-t') \int_\tau^{t'} dt' \sigma'_m(t-\tau')\sigma'_n(\tau-\tau') + \theta(t'-\tau)\sigma_k(\tau-\tau) \int_\tau^{t'} dt' \sigma'_m(t-\tau')\sigma'_n(\tau'-t') \right\} \quad (C5)$$

$$g_{mn,n}^{(2)}(t, t'; \tau) = - \sum_k J_{mk}J_{kn}\theta(t-\tau)\theta(t'-\tau)\sigma'_n(t'-\tau) \times \int_\tau^{t'} dt' \sigma'_m(t-\tau')\sigma_k(\tau'-\tau) - \int_\tau^{t'} dt' \sigma'_m(t-t')\delta(t'-\tau) \times \int_t^{t'} dt'' \int_{t''}^{\tau''} dt' \sigma'_n(t'-\tau')\sigma_m(t-\tau'')\sigma_k(\tau''-\tau') \quad (C6)$$

$$g_{mn,m}^{(2)}(t, t'; \tau) = - \sum_k J_{mk}J_{kn}\theta(t-\tau)\theta(t'-\tau)\sigma'_m(\tau-t) \times \int_\tau^{t'} dt' \sigma'_k(\tau-\tau')\sigma_n(\tau'-t') - \sum_k J_{mk}J_{kn}\theta(t'-t)\delta(t-\tau) \times \int_\tau^{t'} dt'' \int_t^{\tau''} dt' \sigma'_m(\tau'-t)\sigma_k(\tau'-\tau'')\sigma_n(\tau''-t') \quad (C7)$$

$$g_{mn,n}^{(2)}(t, t'; \tau) = - \sum_m J_{mn}J_{mn}\theta(t-\tau)\theta(t'-\tau) \times \left\{ \int_\tau^{t'} dt' \sigma'_m(\tau'-\tau)\Gamma'_n(t', t, \tau', \tau) + \int_\tau^{t'} dt' \sigma'_m(\tau-\tau')\Gamma'_n(\tau, \tau', t', t) \right\}$$

$$- \sum_m J_{mn}J_{mn}\theta(t-t')\delta(t'-\tau) \int_t^{t'} dt'' \int_{t''}^{\tau''} dt' \sigma'_m(\tau''-\tau')\Gamma'_n(t', t, \tau'', \tau') - \sum_m J_{mn}J_{mn}\theta(t-t)\delta(t-\tau) \int_t^{t'} dt'' \int_t^{\tau''} dt' \sigma'_m(\tau'-\tau'')\Gamma'_n(\tau', \tau'', t', t) + \sum_m J_{mn}J_{mn} \int_\tau^\infty dt'' \int_\tau^{\tau''} dt' \sigma_{mn}^{(0)}(t, t'; \tau'') [\sigma_m(\tau'-\tau)\sigma'_n(\tau'-\tau) + \sigma_m(\tau-\tau')\sigma'_n(\tau-\tau')] \quad (C8)$$

$$g_{mn,n}^{(2)}(t, t'; \tau) = J_{mn}J_{mn}\theta(t-\tau)\theta(t'-\tau) \times \left\{ \int_\tau^{t'} dt' \sigma'_n(\tau'-\tau)\Gamma_m(\tau', t', t, \tau) + \int_\tau^{t'} dt' \sigma'_n(\tau-\tau')\Gamma_m(\tau, t', t, \tau') \right\} - \theta(t-\tau)\theta(t'-\tau') \int_\tau^\infty dt'' \int_\tau^{\tau''} dt' \sigma_{mn}^{(0)}(t, t'; \tau'') K_{mn}(\tau'-\tau) \quad (C9)$$

The single-molecule correlation functions  $\sigma_m, \sigma'_m, \Gamma_m$ , and  $\Gamma'_m$  are defined and evaluated in Appendix A. We have also used the following convention: different indices in the l.h.s. of the expressions adopt different values. The same convention will be used in Appendices D and E.

## APPENDIX D: The Doorway Function

In this appendix we calculate the doorway function  $f_{m,nk}(t; \tau, \tau')$  perturbatively up to the second order in  $J$ . We make use of Eqs. (5.16) and (5.14) and apply the procedure of calculating the traces presented in Appendix B which leads to the following expansion:

$$f = f^{(0)} + f^{(1)} + f^{(2)} \quad (D1)$$

with

$$f_{m,nmn}^{(0)}(t; \tau, \tau') = [\theta(\tau'-\tau)\delta(t-\tau') + \theta(\tau-\tau')\delta(t-\tau)] \times \sigma_m(\tau'-\tau) \quad (D2)$$

$$f_{m,nmn}^{(1)}(t; \tau, \tau') = iJ_{mn}\theta(t-\tau)\theta(t-\tau')\sigma_m(t-\tau)\sigma_n(\tau'-t) + iJ_{mn}\theta(\tau-\tau')\delta(t-\tau) \int_\tau^{\tau'} dt' \sigma'_m(t'-\tau)\sigma_n(\tau'-t') \quad (D3)$$

$$-\int d\tau'' dt'' g_{mn,m}^{(1)}(t, t'; \tau'') f^{(0)}(t''; \tau, \tau') \theta(\tau'' - t'') \quad (E8)$$

$$C_{mn,mk}^{(1)}(t, t'; \tau, \tau') = i J_{km} \theta(t - \tau) \theta(t' - \tau') \int_{\tau'}^{t'} d\tau'' \sigma_k(\tau' - \tau'') \Gamma_m(\tau'', t', t, \tau) \\ - \int d\tau'' dt'' g_{mn,m}^{(0)}(t, t'; \tau'') f_{m,mk}^{(1)}(\tau''; \tau, \tau') \theta(\tau'' - t'') \quad (E9)$$

$$C_{mn,k}^{(2)}(t, t'; \tau, \tau') = J_{mk} J_{kn} \theta(t - \tau) \theta(t' - \tau') \int_{\tau}^{t'} dt'' \sigma_m(t - t'') \sigma_k(t'' - \tau) \\ \times \int_{\tau'}^{t''} d\tau'' \sigma_l(\tau' - \tau'') \sigma_n(\tau'' - t') \quad (E10)$$

$$C_{mn,ml}^{(2)}(t, t'; \tau, \tau') = - \sum_{k \neq m} J_{lk} J_{kn} \theta(t - \tau) \theta(t' - \tau') \sigma_m(t - \tau)$$

$$\times \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' \sigma_l(\tau' - \tau'') \sigma_k(\tau'' - t'') \sigma_n(t'' - t') \\ - J_{lm} J_{ml} \theta(t - \tau) \theta(t' - \tau') \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' \\ \times \sigma_l(\tau' - \tau'') \sigma_n(t'' - t') \Gamma_m(\tau'', t'', t, \tau) - \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' g_{mn,m}^{(1)}(t, t'; t'') f_{m,ml}^{(1)}(\tau''; \tau, \tau') \quad (E11)$$

$$C_{mn,kn}^{(2)}(t, t'; \tau, \tau') = - \sum_{l \neq n} J_{ml} J_{lk} \theta(t - \tau) \theta(t' - \tau') \sigma_n(\tau' - t') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_m(t - t'') \sigma_l(t'' - \tau'') \sigma_k(\tau'' - \tau) \\ - J_{mn} J_{nk} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_m(t - t'') \sigma_k(\tau'' - \tau) \Gamma_n(\tau', t', t'', \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' g_{mn,m}^{(1)}(t, t'; t'') f_{n,kn}^{(1)}(\tau''; \tau, \tau') \quad (E12)$$

$$C_{mn,mn}^{(2)}(t, t'; \tau, \tau') = - \sum_k J_{nk} J_{km} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' \sigma_n(\tau' - \tau'') \sigma_k(\tau'' - t'') \Gamma_m(t'', t', t, \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \int_{\tau'}^{t'} dt'' \\ \times \int_{\tau'}^{t''} d\tau'' g_{mn,m}^{(0)}(t, t'; t'') f_{n,mn}^{(2)}(\tau''; \tau, \tau') \quad (E13)$$

$$C_{mn,mn}^{(2)}(t, t'; \tau, \tau') = - \sum_k J_{mk} J_{kn} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_k(t'' - \tau'') \sigma_n(\tau'' - \tau) \Gamma_m(\tau', t', t, t'') \quad (E13)$$

$$-\theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' g_{mn,m}^{(0)}(t, t'; t'') f_{m,mn}^{(2)}(\tau''; \tau, \tau') \quad (E14)$$

$$C_{mn,mn}^{(2)}(t, t'; \tau, \tau') = - \sum_k J_{mk} J_{kn} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' \sigma_k(\tau'' - t'') \sigma_n(t'' - t') \Gamma_m(\tau', \tau'', t, \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau'}^{t'} dt'' \int_{\tau'}^{t''} d\tau'' g_{mn,m}^{(2)}(t, t'; t'') f_{m,mn}^{(0)}(\tau''; \tau, \tau') \quad (E15)$$

$$C_{mn,mn}^{(2)}(t, t'; \tau, \tau') = - \sum_k J_{nk} J_{km} \theta(t - \tau) \theta(t' - \tau')$$

$$\times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_n(t - t'') \sigma_k(t'' - \tau'') \Gamma_m(\tau', t', \tau'', \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \int_{\tau}^{t'} dt'' \\ \times \int_{\tau}^{t''} d\tau'' g_{mn,m}^{(2)}(t, t'; t'') f_{m,mn}^{(0)}(\tau''; \tau, \tau') \quad (E16)$$

$$C_{mk,lm}^{(2)}(t, t'; \tau, \tau') = J_{ml} J_{mk} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_l(t'' - \tau) \sigma_k(\tau'' - t'') \Gamma_m(\tau', \tau'', t, t'') \\ - \theta(t - \tau) \theta(t' - \tau') \int_{\tau}^{t'} dt'' \\ \times \int_{\tau}^{t''} d\tau'' \theta(\tau'' - t'') g_{mk,m}^{(1)}(t, t'; \tau'') f_{m,lm}^{(1)}(t''; \tau, \tau') \quad (E17)$$

$$C_{km,ml}^{(2)}(t, t'; \tau, \tau') = J_{lm} J_{km} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \sigma_k(t - t'') \sigma_l(\tau' - \tau'') \Gamma_m(\tau'', t', t'', \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \theta(t'' - \tau'') g_{km,m}^{(1)}(t, t'; t'') f_{m,ml}^{(1)}(\tau''; \tau, \tau') \quad (E18)$$

$$C_{mn,mn}^{(2)}(t, t'; \tau, \tau') = J_{mn} J_{mn} \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \Gamma_m(\tau', \tau'', t, t'') \Gamma_n(\tau'', t', t'', \tau) \\ - \theta(t - \tau) \theta(t' - \tau') \\ \times \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} d\tau'' \theta(t'' - \tau'') g_{mn,m}^{(1)}(t, t'; t'') f_{n,mn}^{(1)}(\tau''; \tau, \tau') \\ - \theta(t - \tau) \theta(t' - \tau')$$

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