

# Energy transfer, spectral diffusion, and fluorescence of molecular aggregates: Brownian oscillator analysis

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## Abstract

The energy transfer rate and the time- and frequency-resolved fluorescence of molecular dimers is calculated. Spectral diffusion and the time-dependent Stokes shift are incorporated using the Brownian oscillator model for the solvent. The results generalize Förster's energy transfer theory to the case when the energy transfer and spectral diffusion rates are comparable. Generalized rate equations for the excited state populations which contain time-dependent energy transfer rate  $W(t)$  are derived. This rate is expressed in terms of the overlap of the time-dependent fluorescence spectrum of the donor and the absorption spectrum of the acceptor.

## 1. Introduction

Ever since the pioneering works of Förster [1] and Dexter [2], intermolecular energy transfer has been the subject of numerous theoretical and experimental studies [3–5]. In the Förster theory, the time evolution of the excited state populations of two molecules  $n_a(t)$  ( $a = 1, 2$ ), coupled by an intermolecular dipole–dipole interaction with a matrix element  $v$ , is described by the simple rate equations:  $dn_2/dt = -dn_1/dt = W_F n_1(t)$ . Förster has shown that the energy transfer rate constant  $W_F$  can be expressed through the fluorescence lineshape of the first (donor) molecule,  $f_1(\omega)$ , and the absorption lineshape of the second (acceptor),  $a_2(\omega)$ ,

$$W_F = v^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} a_2(\omega) f_1(\omega), \quad (1.1)$$

where both lineshapes are normalized to a unit area,

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f_1(\omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} a_2(\omega) = 1.$$

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Förster's theory holds when intermolecular energy transfer is slow compared to vibrational and solvent relaxation rates  $W_{\text{rel}}$ ,  $W_F \ll W_{\text{rel}}$ , so that the donor's nuclear degrees of freedom are fully relaxed in its excited electronic state prior to the energy transfer process. The fluorescence is given by

$$I_F^{(a)}(\omega, t) = f_a(\omega)n_a(t), \quad a = 1, 2, \quad (1.2)$$

where the fluorescence lineshape  $f_a(\omega)$  is time independent.

In this Letter, we calculate the fluorescence spectra and energy transfer in a molecular dimer, when the transfer rate is comparable to or faster than the nuclear relaxation (solvent reorganization) rate. Recently time-resolved fluorescence and nonlinear optical measurements in the photosynthetic reaction center and in the antenna systems have raised many interesting issues related to the interpretation of coherent and incoherent energy transfer and their spectroscopic signatures [6–8]. When the transfer rate is comparable to the relaxation rate, the time evolution of the system cannot be described by ordinary rate equations, and we need to calculate the two-time dipole correlation functions of the dimer. Moreover, in contrast to Förster's limit, the fluorescence lineshape does change with time due to spectral diffusion processes and may not be related to the excited state population by the simple formula (1.2). By expanding the two-time dipole correlation functions of a dimer perturbatively in the intermolecular interaction, we relate them to multi-time correlation functions of the individual molecules. We then use the Brownian oscillator model [9] which allows us to evaluate the necessary correlation functions for a solvent with an arbitrary spectral density, and derive explicit expressions for the fluorescence spectrum. Finally, we show that at long times the energy transfer process can be described by generalized rate equations with a time-dependent rate  $W(t)$ , which reduces to Förster's rate  $W_F$  when the energy transfer is slow compared to the spectral diffusion timescale.

## 2. Correlation functions for optical response and energy transfer

We consider a molecular dimer whose Hamiltonian is given by

$$H(t) = H_0 + V + \mu[E(t)B_1^- + E^*(t)B_1]. \quad (2.1)$$

Here  $H_0$  is the Hamiltonian of the noninteracting molecules, each assumed to be a two-level electronic system with a ground state  $|g\rangle$  and an excited state  $|e\rangle$ ,

$$H_0 = H_0^{(1)} + H_0^{(2)}, \quad (2.2)$$

$$H_0^{(a)} = H_e^{(a)}B_a^+B_a + H_g^{(a)}B_aB_a^+, \quad a = 1, 2. \quad (2.3)$$

The operators  $B_a^+$  ( $B_a$ ), which create (annihilate) an electronic excitation, obey the Pauli commutation rules,

$$B_aB_b^+ - B_b^+B_a = \delta_{ab}(1 - 2B_b^+B_a), \quad (2.4)$$

where  $\delta_{ab}$  is the Kroneker delta. The nuclear Hamiltonians  $H_g^{(a)}$  and  $H_e^{(a)}$  represent intramolecular and solvent degrees of the freedom.  $V$  represents the intermolecular coupling,

$$V = v(B_1^+B_2 + B_2^+B_1), \quad (2.5)$$

and the last term describes the interaction of the first molecule with an external electric field  $E(t)$ .

The time-resolved fluorescence spectrum of molecule 2 induced by its coupling to molecule 1, which in turn is excited optically is formally given by Refs. [10,11] (see Appendix),

$$I_F(t, \omega) \approx 2\pi\omega \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} P_2(t, t - \tau), \quad (2.6)$$

where

$$P_2(t, t') = \langle \tilde{B}_2^\dagger(t') \tilde{B}_2(t) \rangle, \quad \langle \dots \rangle = \text{Tr}[\dots e^{-H_0/T}] / \text{Tr}[e^{-H_0/T}], \quad (2.7)$$

and  $\tilde{B}_2(t)$  denotes the operators in the Heisenberg representation. To second order in  $v$  we obtain the following relation between  $P_2(t, t')$  and  $P_1(\tau, \tau')$ :

$$P_2(t, t') = v^2 \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' \gamma_2(t, t'; \tau, \tau') P_1(\tau, \tau'). \quad (2.8)$$

A similar calculation for the first molecule results in

$$P_1(t, t') = \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' \gamma_1(t, t'; \tau, \tau') E^*(\tau') E(\tau). \quad (2.9)$$

Here

$$\gamma_a(t, t'; \tau, \tau') = \langle B_a(\tau') B_a^\dagger(t') B_a(t) B_a^\dagger(\tau) \rangle, \quad (2.10)$$

$$B_a(t) = e^{iH_0^{(a)}t} B_a e^{-iH_0^{(a)}t} = e^{iH_g^{(a)}t} e^{-iH_e^{(a)}t} B_a, \quad a = 1, 2. \quad (2.11)$$

The correlation function  $P_1$  acts as an effective external field inducing the fluorescence of the second molecule. We have thus expressed the fluorescence signal of the second molecule to second order in intermolecular coupling, in terms of the four-point correlations functions which determine the fluorescence spectra of the individual molecules [9].

These results can be extended immediately to larger aggregates with an arbitrary number of molecules. We then have

$$P_n(t, t') = \sum_{m \neq n} v_{nm}^2 \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' \gamma_n(t, t'; \tau, \tau') [P_m(\tau, \tau') - E_n^*(\tau') E_n(\tau)]. \quad (2.12)$$

These equations need to be solved for  $P_n(t, t')$ , assuming that the correlations functions  $\gamma_n$  and the field amplitudes  $E_n$  are known. For linear aggregates, and assuming that the field couples to one molecule and that the energy transfer occurs between nearest neighbors, we can solve these equations successively (first calculate  $P_1$ , then  $P_2$ , etc.).

### 3. Application to the Brownian oscillator model

In what follows we describe the solvent effects using the Brownian oscillator model [9,12,13]. In this model, nuclear motions that couple to the electronic transition are modeled as harmonic modes whose equilibrium positions are displaced between the two electronic states. The Hamiltonians  $H_g^{(a)}$  and  $H_e^{(a)}$  assume the form

$$H_g^{(a)} = \sum_j \omega_j^{(a)} b_j^{(a)\dagger} b_j^{(a)}, \quad (3.1)$$

$$H_e^{(a)} = \omega_{eg}^{(a)} + \frac{1}{2} \sum_j \omega_j^{(a)} (d_j^{(a)})^2 + \frac{1}{\sqrt{2}} \sum_j \omega_j^{(a)} d_j^{(a)} (b_j^{(a)\dagger} + b_j^{(a)}) + \sum_j \omega_j^{(a)} b_j^{(a)\dagger} b_j^{(a)}, \quad (3.2)$$

where  $\omega_{\text{eg}}^{(a)}$  is the electronic transition frequency,  $\omega_j^{(a)}$ ,  $d_j^{(a)}$  are the frequency and the dimensionless displacement of the  $j$ th oscillator. This model is closely related to the spin-Boson Hamiltonian used in the theory of electron transfer [14–16]. The existence of two collective solvent coordinates is similar to the problem of multisite electron transfer (e.g. the superexchange problem) [17].

Using this model, we can calculate the necessary two- and four-point correlation functions. We then have

$$\sigma(t-t') \equiv \langle B(t)B^+(t') \rangle = \exp[-i(\omega_{\text{eg}} + \lambda)(t-t') - g(t-t')], \quad (3.3)$$

with

$$\lambda = \frac{1}{2} \sum_j d_j^2 \omega_j.$$

The function  $g(t)$  is given by

$$g(t) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{C(\omega)}{\omega^2} \left[ [1 - \cos(\omega t)] \coth\left(\frac{\omega}{2k_B T}\right) - i[\sin(\omega t) - \omega t] \right], \quad (3.4)$$

where  $C(\omega)$  is the spectral density associated with nuclear solvent and intramolecular dynamics,

$$C(\omega) = \frac{1}{2} \sum_j \omega_j^2 d_j^2 [\delta(\omega - \omega_j) - \delta(\omega + \omega_j)], \quad (3.5)$$

and  $k_B$  is the Boltzmann constant.

The absorption and fluorescence lineshapes are given by the Fourier transform of the two-point correlation function  $\sigma(t)$ ,

$$a(\omega) = \int_{-\infty}^{\infty} dt \exp[i(\omega - \omega_{\text{eg}} - \lambda)t - g(t)], \quad (3.6)$$

$$f(\omega) = \int_{-\infty}^{\infty} dt \exp[i(\omega - \omega_{\text{eg}} - \lambda)t - g^*(t)]. \quad (3.7)$$

The four-point correlation function  $\gamma$  which determines the time-resolved fluorescence spectrum is given by

$$\gamma_a(t, t'; \tau, \tau') = \exp[-i(\omega_{\text{eg}} + \lambda)(t - t' + \tau' - \tau) - F(t, t'; \tau, \tau')], \quad (3.8)$$

where

$$F(t, t'; \tau, \tau') = g(t - \tau) + g(\tau' - t') + g(t' - t) + g(\tau' - \tau) - g(t' - \tau) - g(\tau' - t). \quad (3.9)$$

In condensed phases it is possible to represent the solvent dynamics in terms of a continuous distribution of oscillators. By changing the summation over oscillator modes in the above expressions to integration, and assuming the following form for the spectral density of the oscillator system:

$$C(\omega) = 2\lambda \frac{\omega A}{\omega^2 + A^2} \quad (3.10)$$

one finds in the high temperature limit,  $k_B T \gg A$ ,

$$g(t) = \left( \frac{A^2}{A^2} - i \frac{\lambda}{A} \text{sgn}(t) \right) (e^{-|t|} + A|t| - 1), \quad (3.11)$$

where

$$\Delta^2 = \frac{1}{2} \sum_j d_j^2 \omega_j^2 \coth\left(\frac{\omega_j}{2T}\right) \approx 2\lambda k_B T, \quad k_B T \gg A. \quad (3.12)$$

The correlation function (3.3) determines the absorption and the relaxed fluorescence spectra of a molecule. In the case of the static (inhomogeneous, slow modulation) limit,  $\Delta \gg A$ , the function  $g(t)$  takes the form

$$g(t) = \frac{1}{2} \Delta^2 t^2, \quad (3.13)$$

and the absorption and fluorescence lineshapes assume the Gaussian profiles,

$$a(\omega) = \left(\frac{2\pi}{\Delta^2}\right)^{1/2} \exp\left(-\frac{(\omega - \omega_{cg} - \lambda)^2}{2\Delta^2}\right), \quad (3.14)$$

$$f(\omega) = \left(\frac{2\pi}{\Delta^2}\right)^{1/2} \exp\left(-\frac{(\omega - \omega_{cg} + \lambda)^2}{2\Delta^2}\right). \quad (3.15)$$

These expressions show that the fluorescence maximum is shifted by  $2\lambda$  (the Stokes shift) to the red relative to the absorption maximum [14].

We next summarize some results of the Brownian oscillator model in the static limit,  $\Delta \gg A$ . These will be used in Section 4 for the description of the dimer fluorescence. The function  $F$  (3.8) is the sum of six  $g$ -functions which depend on several time intervals. In the static limit the time intervals  $|t - t'| \sim \Delta^{-1}$  and  $|\tau - \tau'| \sim \Delta^{-1}$  are much shorter than  $A^{-1}$ , and one can use the expression (3.13) for the functions  $g(t - t')$  and  $g(\tau - \tau')$ . The function

$$F = g(t - t') + g(\tau' - \tau) + g(t - \tau) + g[(\tau - t) - (t' - t) - (\tau - \tau')] - g[(t - \tau) + (t' - t)] - g[(\tau - t) + (\tau' - \tau)] \quad (3.16)$$

can be expanded in the Taylor series in powers  $A(t - t')$  and  $A(\tau' - \tau)$ ,

$$F(t, t'; \tau, \tau') = \frac{1}{2} \Delta^2 (t - t')^2 + \frac{1}{2} \Delta^2 (\tau' - \tau)^2 - 2i\lambda(t - t') [1 - e^{-A(t - \tau)}] + \Delta^2 (t - t')(\tau - \tau') e^{-A(t - \tau)}. \quad (3.17)$$

In the limit  $A(t - \tau) \gg 1$  the function  $F$  takes the form

$$F(t, t'; \tau, \tau') = \frac{1}{2} \Delta^2 (t - t')^2 + \frac{1}{2} \Delta^2 (\tau' - \tau)^2 - 2i\lambda(t - t'), \quad (3.18)$$

and, hence, the four-point correlation function is factorized into the product of the two-point correlation functions

$$\gamma(t, t'; \tau, \tau') = \sigma_f(t - t') \sigma(\tau' - \tau), \quad (3.19)$$

$$\sigma_f(t - t') = \exp[-i(\omega_{cg} - \lambda)(t - t') - \frac{1}{2} \Delta^2 (t - t')^2], \quad (3.20)$$

$$\sigma(\tau' - \tau) = \exp[-i(\omega_{cg} + \lambda)(\tau' - \tau) - \frac{1}{2} \Delta^2 (\tau' - \tau)^2]. \quad (3.21)$$

Here the index  $f$  shows that the Fourier transform of the function  $\sigma_f(t)$  gives the relaxed fluorescence lineshape (3.15). Substituting these expressions in (2.9), we recover the Förster limit (1.2),

$$I_f(t, \omega) = f(\omega) n(t), \quad (3.22)$$

where

$$n(t) = \mu^2 \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \sigma(\tau_2) E^*(\tau_1 + \tau_2) E(\tau_1) \quad (3.23)$$

is the excited state population of the molecule driving by the external field.

#### 4. Time- and frequency-resolved fluorescence at long times

We now assume that the characteristic intermolecular energy transfer rate,  $W$ , is much smaller than the inhomogeneous linewidth  $\Delta$ , but can be comparable to the inverse solvent timescale  $\Lambda$ . In this case, we can focus on the long-time behavior ( $\frac{1}{2}(t+t') \gg \Delta^{-1}$ ) of the correlation functions  $P_a(t, t')$ . Because the main contribution to the integrals in (2.8), (2.9) comes from the vicinity of  $|\tau - \tau'| \sim \Delta_1^{-1}, \Delta_2^{-1}$ , they can be recast as follows:

$$P_2(t, t-t') = v^2 \int_{-\infty}^t d\tau \int_{-\infty}^{\infty} d\tau' \gamma_2(t, t', \tau, \tau') P_1(\tau, \tau - \tau'), \quad (4.1)$$

$$P_1(t, t-t') = \int_{-\infty}^t d\tau \int_{-\infty}^{\infty} d\tau' \gamma_1(t, t', \tau, \tau') E^*(\tau) E(\tau'). \quad (4.2)$$

Here we assume that the correlation functions  $\gamma_{1,2}(t, t', \tau, \tau')$  are given by the expressions (3.8) and (3.17). In Eq. (4.2) we also assumed that the incident pulse is much shorter than  $W^{-1}$  and omitted  $\tau$  in the argument  $t - \tau$  of the correlation function  $\gamma_1$ .

The excited state population of the first molecule is given by

$$n_1(t) \equiv P_1(t, 0) = \int_{-\infty}^{\infty} d\tau_1 a_1(\tau_1) \int_{-\infty}^t d\tau E^*(\tau + \tau_1/2) E(\tau - \tau_1/2), \quad (4.3)$$

where

$$a_1(\tau) = \exp[-i(\omega_{\text{eg}}^{(1)} + \lambda)\tau - \frac{1}{2}\Delta_1^2 \tau^2]. \quad (4.4)$$

The Fourier transform of the function  $a_1(\tau)$ ,

$$a_1(\omega) = \int_{-\infty}^{\infty} d\tau a_1(\tau) e^{i\omega\tau} = \left(\frac{2\pi}{\Delta_1^2}\right)^{1/2} \exp\left(-\frac{(\omega - \omega_{\text{eg}}^{(1)} - \lambda)^2}{2\Delta_1^2}\right), \quad (4.5)$$

is the absorption spectrum of the first molecule.

For a Gaussian incident field,

$$E(\tau) = E_0 \exp(-i\Omega\tau - \kappa^2\tau^2), \quad (4.6)$$

we find for the correlation function  $P_1$ ,

$$P_1(t, t-t') = f_1(t, t-t') n_1(t), \quad (4.7)$$

where

$$n_1(t) = \mu^2 E_0^2 \left( \frac{2\pi}{\Delta_1^2 + \kappa^2} \right)^{1/2} \exp \left( -\frac{(\Omega - \omega_{\text{eg}}^{(1)} - \lambda_1)^2}{2(\Delta_1^2 + \kappa^2)} \right) \int_{-\infty}^t d\eta e^{-2k^2\eta^2}, \quad (4.8)$$

$$f_1(t, t - t') = \exp \left[ -i\omega_1(t)(t - t') - \frac{1}{2}b_1^2(t)(t - t')^2 \right], \quad (4.9)$$

$$\omega_1(t) = \omega_{\text{eg}}^{(1)} - \lambda_1 [1 - 2M_1(t)] + (\Omega - \omega_{\text{eg}}^{(1)} - \lambda_1) \frac{\Delta_1^2}{\Delta_1^2 + \kappa^2} M_1(t), \quad (4.10)$$

$$b_1^2(t) = \Delta_1^2 \left( 1 - \frac{\Delta_1^2}{\Delta_1^2 + \kappa^2} M_1^2(t) \right), \quad (4.11)$$

$$M_1(t) = \exp(-A_1 t). \quad (4.12)$$

The Fourier transform of  $f_1(t, t - t')$ ,

$$f_1(t, \omega) = \int_{-\infty}^{\infty} d\tau f_1(t, \tau) e^{i\omega\tau} = \left( \frac{2\pi}{b_1^2(t)} \right)^{1/2} \exp \left( -\frac{[\omega - \omega_1(t)]^2}{2b_1^2(t)} \right), \quad (4.13)$$

describes a time-dependent (non-equilibrium) fluorescence spectrum of the first molecule, whose maximum and width change with time.

Inserting (4.7) into (4.1) we can express the correlation function  $P_2$  through the population of the first molecule,

$$P_2(t, t - t') = \int_{-\infty}^t dt_1 f_2(t, t - t'; t_1) W(t_1) n_1(t_1), \quad (4.14)$$

where

$$f_2(t, t - t'; t_1) = \exp \left[ -i\omega_2(t, t_1) - \frac{1}{2}b_2^2(t, t_1)\xi^2 \right], \quad (4.15)$$

$$\omega_2(t, t_1) = \omega_{\text{eg}}^{(2)} - \lambda_2 [1 - 2M_2(t - t_1)] \quad (4.16)$$

$$+ [\omega_1(t_1) - \omega_{\text{eg}}^{(2)} - \lambda_2] \frac{\Delta_2^2}{\Delta_2^2 + b_2^2(t_1)} M_2(t - t_1), \quad (4.17)$$

$$b_2^2(t, t_1) = \Delta_2^2 \left( 1 - \frac{\Delta_2^2}{\Delta_2^2 + b_1^2(t_1)} M_2^2(t - t_1) \right), \quad (4.18)$$

$$M_2(t) = \exp(-A_2 t). \quad (4.19)$$

$f_2$  describes a time-dependent fluorescence spectrum of the second molecule, while

$$W(t) = \nu^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} a_2(\omega) f_1(\omega, t) \quad (4.20)$$

represents the overlap of the absorption spectrum of the acceptor and the time-dependent fluorescence spectrum of the donor. Eq. (4.20) is a simple generalization of Förster rate (Eq.(1.1)) to include the time-dependent Stokes shift. For our model we find

$$W(t) = v^2 \left( \frac{2\pi}{\Delta_2^2 + b_1^2(t)} \right)^{1/2} \exp \left( - \frac{[\omega_1(t) - \omega_{eg}^{(2)} - \lambda_2]^2}{2[\Delta_2^2 + b_1^2(t)]} \right). \quad (4.21)$$

Within the Brownian oscillator model we thus obtained explicit expressions (4.7), (4.14) for the time-dependent fluorescence spectra of both molecules to second order in the intermolecular coupling.

Finally we show how our results generalize Förster's theory to the case of non-equilibrium energy transfer, by introducing a time-dependent rate. A time-dependent rate has been used in the definition of the analogues problem of electron transfer in Refs. [18–20]. Setting  $t = t'$  in Eq. (4.14), we find for the population of the second molecule,

$$n_2(t) \equiv P_2(t, 0) = \int_{-\infty}^t dt_1 W(t_1) n_1(t_1). \quad (4.22)$$

Hence, the fluorescence spectrum of the acceptor can be rewritten in the form

$$I_2(\omega, t) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} P_2(\tau, t) = \int_{-\infty}^t dt_1 f_2(t, t_1) \frac{d}{dt_1} n_2(t_1). \quad (4.23)$$

The excited state populations can be obtained as the solution of the following set of the equations:

$$\frac{d}{dt} n_2(t) = W(t) n_1(t), \quad (4.24)$$

$$\frac{d}{dt} n_1(t) = I(t) - W(t) n_1(t), \quad (4.25)$$

where  $I(t)$  is the overlap of the spectrum of the incident Gaussian field and the absorption spectrum of the first molecule,

$$I(t) = \mu^2 E_0^2 \left( \frac{2\pi}{\Delta_1^2 + k^2} \right)^{1/2} \exp \left( - \frac{(\Omega - \omega_{eg}^{(1)} - \lambda_1)^2}{2(\Delta_1^2 + k^2)} \right) e^{-2k^2 t^2}. \quad (4.26)$$

These expressions generalize Förster's formula (1.2) to the case of hot (unrelaxed) fluorescence. In the limit  $At \gg 1$  the function  $M_1(t) \rightarrow 0$ , and we recover Förster's rate equations with the Förster rate  $W_F = W(t \rightarrow \infty)$ .

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## Appendix A

In the Appendix we derive the basic expressions for the correlation functions (2.8) and (2.9) to second order in the external field. The time-resolved fluorescence spectrum of molecule 2 induced by its coupling to molecule 1, which in turn is excited by an external electromagnetic field is formally given by Refs. [10,11],



$$I_F(t, \omega) = 2\pi\omega \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi i} \frac{d\omega'}{2\pi} \frac{\omega' e^{-i\omega' t}}{(\epsilon - \omega - i0)(\epsilon + \omega' - \omega + i0)} P_2(\epsilon + \omega', \omega'). \quad (\text{A.1})$$

Here

$$P_2(\epsilon + \omega, \omega) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt dt' \exp\{i[(\epsilon + \omega)t - \epsilon t']\} P_2(t, t') \quad (\text{A.2})$$

is the double Fourier transform of the correlation function (Eq. (2.7))

If the temporal evolution of the spectrum is slow (typical timescale longer than the inverse linewidth) one can evaluate the integral (A.1) over  $\epsilon$  by only taking into account the contribution in the pole  $\epsilon = \omega + i0$ . We then find

$$I_F(t, \omega) \approx 2\pi\omega \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} e^{-i\omega' t} P_2(\omega + \omega', \omega') = 2\pi\omega \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} P_2(t, t - \tau), \quad (\text{A.3})$$

where  $\tau = t - t'$ . This is an ideal spectrum. The actual observed spectrum may be calculated by convoluting  $I_F(t, \omega)$  with spectral and temporal gate functions related to the detection device [21].

To evaluate the correlation function  $P_2(t, t')$  we use the Keldysh representation [22,23] for non-equilibrium correlations functions.  $P_2(t, t')$  is a chronologically ordered averaged value on the Keldysh loop that goes from the  $t = -\infty$  to the  $t = +\infty$  and back,

$$P_2^{(-+)}(t, t') = \langle T_C[\bar{B}_2^+(t') \bar{B}_2(t)] \rangle. \quad (\text{A.4})$$

Here the indexes (+) and (-) indicate that the time argument lies on the positive (from  $-\infty$  to  $+\infty$ ) or negative (from  $+\infty$  to  $-\infty$ ) branches of the Keldysh loop. Expanding Eq. (A.6) to second order in the external field, we find

$$P_2(t, t') = \mu^2 \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\tau' K(t, t'; \tau, \tau') E^*(\tau') E(\tau), \quad (\text{A.5})$$

$$K(t, t'; \tau, \tau') = \langle [\bar{T} \bar{B}_1(\tau') \bar{B}_2^+(t')] [T \bar{B}_2(t) \bar{B}_1^+(\tau)] \rangle, \quad (\text{A.6})$$

where the overbar in  $\bar{B}_a(t)$  denotes the time evolution with respect to the free dimer Hamiltonian,

$$\bar{B}_a(t) \equiv e^{i(H_0 + V)t} B_a e^{-i(H_0 + V)t}. \quad (\text{A.7})$$

$\bar{T}$  and  $T$  stand for anti-chronological and chronological time ordering, respectively. Expanding the correlation function  $K(t, t'; \tau, \tau')$  to second order in intermolecular coupling  $v$ , we obtain

$$K(t, t'; \tau, \tau') = v^2 \int_{-\infty}^{\infty} dt_1 dt_2 \Gamma_2(t, t'; t_1, t_2) \Gamma_1(t_1, t_2; \tau, \tau'), \quad (\text{A.8})$$

where

$$\Gamma_a(t, t'; \tau, \tau') = \langle [\bar{T} B_a(\tau') B_a^-(t')] [T B_a(t) B_a^+(\tau)] \rangle, \quad (\text{A.9})$$

$$= \gamma_a(t, t'; \tau, \tau') \theta(t - \tau) \theta(t' - \tau') \quad (\text{A.10})$$

and

$$\gamma_a(t, t'; \tau, \tau') = \langle B_a(\tau') B_a^\dagger(t') B_a(t) B_a^\dagger(\tau) \rangle, \quad (\text{A.11})$$

$$B_a(t) = e^{iH_0^{(a)}t} B_a e^{-iH_0^{(a)}t} = e^{iH_c^{(a)}t} e^{-iH_c^{(a)}t} B_a, \quad a = 1, 2. \quad (\text{A.12})$$

## References

- [1] Th. Förster, *Ann. Physik (Leipzig)* 2 (1948) 55.
- [2] D.L. Dexter, *J. Chem. Phys.* 21 (1953) 836.
- [3] V.M. Agranovich and M.D. Galanin, *Electronic excitation energy transfer in condensed matter* (North-Holland, Amsterdam, 1982).
- [4] R.S. Knox, in: *Primary processes of photosynthesis*, ed. J. Barber (North-Holland, Amsterdam, 1977) p. 55.
- [5] V.M. Kenkre and P. Reineker, *Exciton dynamics in molecular crystals and aggregates*, in: *Springer tracts in modern physics*, Vol. 94 (Springer, Berlin, 1982).
- [6] W. Holzapfel, U. Finkle, W. Kaiser, D. Oesterhelt, H. Scheer, H.U. Stolz and W. Zinth, *Chem. Phys. Letters* 160 (1989) 1; *Proc. Natl. Acad. Sci. US* 87 (1990) 5168.
- [7] S. Schmidt, T. Arlt, P. Hamm, H. Huber, T. Nägele, J. Wachtveitl, M. Meyer, H. Scheer and W. Zinth, *Chem. Phys. Letters* 223 (1994) 116.
- [8] R. Van Grondelle, J.P. Dekker and V. Sundstrom, *Biochim. Biophys. Acta* 1187 (1994) 1.
- [9] S. Mukamel, *Principles of nonlinear optical spectroscopy* (Oxford Univ. Press, New York, 1995).
- [10] B.R. Mollow, *Phys. Rev.* 188 (1969) 1969.
- [11] V. Chernyak, N. Wang and S. Mukamel, *Phys. Rept.*, to be published.
- [12] W.B. Bosma, Y.J. Yan and S. Mukamel, *Phys. Rev. A* 42 (1990) 6920.
- [13] L.E. Fried and S. Mukamel, *Advan. Chem. Phys.* 84 (1993) 435.
- [14] R.A. Marcus and N. Sutin, *Biochim. Biophys. Acta* 811 (1985) 265.
- [15] A.O. Caldeira and A.J. Leggett, *Physica A* 121 (1983) 587.
- [16] H. Grabert, P. Schramm and G.L. Ingold, *Phys. Rept.* 168 (1988) 115.
- [17] Y. Hu and S. Mukamel, *J. Chem. Phys.* 91 (1989) 6973.
- [18] I. Yu. Tekhver and V.V. Khizhnyakov, *Soviet Phys. JETP* 42 (1976) 305.
- [19] E. Neria and A. Nitzan, *J. Chem. Phys.* 99 (1993) 1109.
- [20] R.D. Coalson, D.G. Evans and A. Nitzan, *J. Chem. Phys.* 101 (1994) 436.
- [21] H. Stolz, *Time-resolved light scattering from excitons* (Springer, Berlin, 1994).
- [22] L.V. Keldysh, *Soviet Phys. JETP* 20 (1965) 1018.
- [23] E.M. Lifshitz and L.P. Pitaevskii, *Physical kinetics* (Pergamon Press, Oxford, 1981) ch. X.