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Time and Frequency Resolved Luminescence from Excitonic Nanostructures

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Time and frequency resolved luminescence spectroscopy of molecular and semiconductor nanostructures provides a direct probe for exciton transport and relaxation. A microscopic Green function theory which incorporates effects of inelastic scattering induced by exciton–phonon interactions, and elastic scattering due to static disorder is developed.

1. Introduction

Effects of geometric confinement on optical properties of nanostructures are currently drawing considerable attention [1, 2]. Molecular aggregates have a relatively simple electronic state structure which can be described by the Frenkel exciton model. Since the exciton bandwidth in molecular crystals is typically much smaller than the molecular transition frequency, one can neglect interactions which do not conserve the number of excitons (the Heitler-London approximation) [3], which greatly simplifies the theoretical modeling. Exciton properties become more complicated if additional degrees of freedom such as nuclear motions are taken into account. Since the number of phonons is not conserved by exciton–phonon interaction, the dynamics of one-exciton states becomes a genuine many-body problem. Another source of nontrivial exciton behavior is static disorder which often exists in molecular aggregates due to the relatively weak intermolecular forces [1, 2, 4].

The simplest optical measurement is linear absorption. This can be expressed in terms of the expectation value of the electric field induced by the material polarization [5], and the signal is proportional to the imaginary part of the linear optical susceptibility. This measurement provides information about interactions of long-wave excitons with energies close to the band edge, which are involved in the absorption, with nuclear motions and disorder which affect the absorption lineshape.

The properties of short-wave excitons (with energies far from the band edge), including exciton transport in momentum space due to exciton–phonon and exciton–disorder scattering, can be studied using either nonlinear optical techniques [6 to 8] or incoherent optical measurements such as time and frequency resolved luminescence [8, 9]. Nonlinear optical measurements provide detailed information about excitons, in particular the dynamics of multi-exciton states (reflecting the direct exciton–exciton interaction). Certain techniques such as degenerate four-wave mixing [10], transient grating [11], and pump–probe spectroscopy [5] can probe the exciton transport properties [6 to 8]. In incoherent optical

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measurements, we look for the signal with frequencies and wave vectors different from the incident light, and exciton transport shows up without the participation of multi-exciton states. The incoherent component of the signal can be expressed in terms of the expectation value of the square of the electric field, whereas the expectation value of the electric field is required for the coherent component.

A formal analogy between four-wave mixing and time and frequency resolved luminescence has been established for the simple model of a single chromophore [12], and then extended for excitonic nanostructures [8]. Recent upconversion femtosecond measurements of spontaneous emission from GaAs quantum wells have raised some interesting theoretical questions [13]. These include their classification as either ‘‘Rayleigh’’ or ‘‘luminescence’’, and the interplay of radiative decay, exciton scattering, and phonons. These problems have much in common with the issue of Raman and fluorescence spectra of dye molecules and molecular aggregates. A proper microscopic description of these effects should allow the formulation of the problem using a combination of four-point correlation functions of the dipole operator. These in turn may be evaluated using Green function techniques. In this paper we present a theoretical study of the time and frequency resolved luminescence from molecular nanostructures, paying particular attention to the signatures of exciton–phonon interactions, disorder, and exciton transport in the time evolution of these spectra.

2. Correlation Function Expressions for Time and Frequency Resolved Luminescence

For the formal definition of the time-dependent emission spectrum we will use the rate of change of the number of photons with a given wave vector \mathbf{k} [5, 12],

$$S_{\text{fl}}(\mathbf{k}, t) \equiv \frac{d}{dt} \langle \hat{a}_{\mathbf{k}}^\dagger(t) \hat{a}_{\mathbf{k}}(t) \rangle, \quad (2.1)$$

where \mathbf{k} is the photon wave vector which determines the frequency of the signal and the direction of observation. $\hat{a}_{\mathbf{k}}$, $\hat{a}_{\mathbf{k}}^\dagger$ are the photon annihilation and creation operators. Other definitions of the time-dependent spectrum which incorporate the detection explicitly, can all be expressed by a proper convolution of (2.1) with frequency and time gate functions [9]. We, therefore, use (2.1) as the primary definition which carries all necessary information about the material system. We assume that the system is driven by an external field $\mathcal{E}(\mathbf{r}, t)$.

Applying the Maxwell equations, the signal in (2.1) can be expressed in terms of a correlation function of the polarization [8],

$$S_{\text{fl}}(\omega_s, t; \mathbf{k}_s) = 2\pi\omega_s \int d\tau \exp(i\omega_s\tau) \mathcal{C}_p \left(\mathbf{k}_s t + \frac{\tau}{2}, -\mathbf{k}_s t - \frac{\tau}{2} \right) \quad (2.2a)$$

with

$$\mathcal{C}_p(\mathbf{k}_1 t_1, \mathbf{k}_2 t_2) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \exp(-i\mathbf{k}_1 \cdot \mathbf{r}_1 - i\mathbf{k}_2 \cdot \mathbf{r}_2) \mathcal{C}_p(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \quad (2.2b)$$

and

$$\mathcal{C}_p(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \equiv \frac{1}{2} [\langle \tilde{\mathcal{P}}(\mathbf{r}_1, t_1) \tilde{\mathcal{P}}(\mathbf{r}_2, t_2) \rangle + \langle \tilde{\mathcal{P}}(\mathbf{r}_2, t_2) \tilde{\mathcal{P}}(\mathbf{r}_1, t_1) \rangle]. \quad (2.2c)$$

ω_s is the signal frequency and \mathbf{k}_s the projection of the emitted photon wave vector on the system and we set $\hbar = 1$. $\tilde{\mathcal{P}}(\mathbf{r}, t)$ denotes the polarization operator in the Heisenberg picture, evolving in time using the Hamiltonian with the external field present.

When expanded to lowest order in the external field, the necessary dipole correlation function assumes the form

$$\mathcal{C}_p(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \int d\mathbf{r}'_1 d\tau'_1 d\mathbf{r}'_2 d\tau'_2 R_c^{(2)}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2; \mathbf{r}'_1 \tau'_1, \mathbf{r}'_2 \tau'_2) \mathcal{E}(\mathbf{r}'_1, \tau'_1) \mathcal{E}(\mathbf{r}'_2, \tau'_2), \quad (2.3)$$

where $R_c^{(2)}$ is a response function which can be written in terms of four-point correlation functions of polarization [8],

$$\begin{aligned} R_c^{(2)}(\mathbf{r}t, \mathbf{r}'t'; \mathbf{r}_1 \tau_1, \mathbf{r}_2 \tau_2) = & \frac{1}{2} \{ \langle T[\hat{P}_R(\mathbf{r}, t) \hat{P}_L(\mathbf{r}', t') \hat{P}_L(\mathbf{r}_1, \tau_1) \hat{P}_L(\mathbf{r}_2, \tau_2)] \rangle \\ & + \langle T[\hat{P}_R(\mathbf{r}, t) \hat{P}_L(\mathbf{r}', t') \hat{P}_R(\mathbf{r}_1, \tau_1) \hat{P}_R(\mathbf{r}_2, \tau_2)] \rangle \\ & - \langle T[\hat{P}_R(\mathbf{r}, t) \hat{P}_L(\mathbf{r}', t') \hat{P}_L(\mathbf{r}_1, \tau_1) \hat{P}_R(\mathbf{r}_2, \tau_2)] \rangle \\ & - \langle T[\hat{P}_R(\mathbf{r}, t) \hat{P}_L(\mathbf{r}', t') \hat{P}_R(\mathbf{r}_1, \tau_1) \hat{P}_L(\mathbf{r}_2, \tau_2)] \rangle + \text{c.c.} \}. \end{aligned} \quad (2.4)$$

Here $\hat{P}(\mathbf{r}, t)$ denotes the polarization evolving in time in the interaction picture representing the isolated system with no external field. In each term, the various P operators need to be ordered using the following prescription: All P_L are placed to the left of the equilibrium density matrix and all P_R are placed to the right. T is a time ordering operator which rearranges the P_L operators in a chronological order and the P_R operators in the reverse (antichronological) order.

3. Application to Nanostructures with Exciton–Phonon Interactions

We now calculate the time-dependent luminescence spectra from molecular assemblies with exciton–phonon interaction. We consider a collection of interacting two-level molecules which further interact with phonons, and the exciton–phonon interaction is taken to be linear in the phonon operators. The matter Hamiltonian \hat{H}_m is [3]

$$\hat{H}_m = \Omega \sum_m \hat{B}_m^\dagger \hat{B}_m + \sum_{m \neq n} J_{mn} \hat{B}_m^\dagger \hat{B}_n + \sum_{m,n} \Omega_{mn} \hat{b}_m^\dagger \hat{b}_n + \sum_{mnl} V_{mnl} \hat{B}_m^\dagger \hat{B}_n (\hat{b}_l^\dagger + \hat{b}_l). \quad (3.1a)$$

The first three terms represent the exciton and the phonon energy, and the fourth is the exciton–phonon interaction. The sum over m and n in the fourth term includes diagonal on-site coupling ($n = m$) as well as off-diagonal ($n \neq m$) coupling. Optical phonons usually couple through the former terms, and acoustic phonons through the latter [3]. \hat{B}_m (\hat{B}_m^\dagger) is the exciton annihilation (creation) operator of the m -th two-level system, which changes its excited state to the ground state. They satisfy the Pauli commutation relations

$$[\hat{B}_m, \hat{B}_n^\dagger] = (1 - 2\hat{B}_m^\dagger \hat{B}_n) \delta_{mn}. \quad (3.1b)$$

Ω_m is the excitation energy of the m -th molecule and J_{mn} the intermolecular coupling which is responsible for exciton hopping.

The polarization operator $\hat{P}(\mathbf{r})$ for our model has the form [8]

$$\hat{P}(\mathbf{r}) = \sum_m \hat{P}_m(\mathbf{r}), \quad (3.2a)$$

$$\hat{P}_m(\mathbf{r}) = |\mu| \rho(\mathbf{r} - \mathbf{R}_m) (\hat{B}_m + \hat{B}_m^\dagger) \quad (3.2b)$$

with ρ representing the distribution of the transition dipole with

$$|\int \rho(\mathbf{r}) d\mathbf{r}| = 1. \quad (3.2c)$$

In the dipole approximation we set $\rho(\mathbf{r}) = \delta(\mathbf{r})$.

In the following we will assume that the system possesses translational symmetry, and consider either infinite d -dimensional lattices with lattice constant a for $d = 1, 2$, or finite d -dimensional lattices with size much smaller than the wavelength, and periodic boundary conditions for $d = 1, 2, 3$. We shall switch to momentum (\mathbf{k}) space, using the following convention. For an arbitrary function f we have for an infinite lattice

$$f(n) = \left(\frac{a}{2\pi}\right)^d \int d^d k f(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_n) \quad (3.3a)$$

and for a lattice with N sites and periodic boundary conditions

$$f(n) = \frac{1}{N} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} f(\mathbf{k}). \quad (3.3b)$$

In the momentum domain, the Hamiltonian assumes the form

$$\begin{aligned} \hat{H}_m = & \int d\mathbf{q} \{ \varepsilon(\mathbf{q}) \hat{B}_q^+ \hat{B}_q + \Omega(\mathbf{q}) \hat{b}_q^+ \hat{b}_q \} \\ & + \int d\mathbf{q} d\mathbf{p} V(\mathbf{q}, \mathbf{q} - \mathbf{p}) \{ \hat{B}_p^+ \hat{B}_q \hat{b}_{q-p}^+ + V^*(\mathbf{q}, \mathbf{q} - \mathbf{p}) \hat{B}_q^+ \hat{B}_p \hat{b}_{q-p} \}, \end{aligned} \quad (3.4a)$$

where $\varepsilon(\mathbf{q})$ is the exciton energy

$$\varepsilon(\mathbf{q}) = \Omega + \sum_n J_{n0} \exp(i\mathbf{q} \cdot \mathbf{R}_n) \quad (3.4b)$$

and

$$V(\mathbf{q}, \mathbf{q} - \mathbf{p}) \equiv \sum_{mm'} \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_l) - i\mathbf{p} \cdot (\mathbf{R}_m - \mathbf{R}_l)] V_{mm'}. \quad (3.4c)$$

Using nonequilibrium Green function techniques [8, 14] we have calculated the correlation function (2.4) and recast the time-dependent spectrum in the form [8]

$$S_{fl}(\omega_s, t; \mathbf{k}_s) = S_{fl}^c(\omega_s, t; \mathbf{k}_s) + S_{fl}^i(\omega_s, t; \mathbf{k}_s), \quad (3.5a)$$

where S_{fl}^c is the coherent component of the signal which has the same frequency and wave vector of the incident light and S_{fl}^i the incoherent component representing the time-dependent spectrum. They are given by

$$\begin{aligned} S_{fl}^c(\omega_s, t; \mathbf{k}_s) = & \mu^4 2\pi \omega_s \delta(\mathbf{k}_s - \mathbf{k}_0) \int \frac{d\omega}{2\pi} \exp(-i\omega t) \\ & \times G\left(\omega_s + \frac{\omega}{2}, \mathbf{k}_s\right) G^*\left(\omega_s - \frac{\omega}{2}, \mathbf{k}_s\right) \mathcal{E}\left(\omega_s + \frac{\omega}{2}\right) \mathcal{E}^*\left(\omega_s - \frac{\omega}{2}\right) \end{aligned} \quad (3.5b)$$

and

$$S_{il}^i(\omega_s, t; \mathbf{k}_s) = \mu^4 2\pi \omega_s \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \times \mathcal{G}_s^{(2)}(\omega' \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) \exp(-i\omega t) \mathcal{E}\left(\omega' + \frac{\omega}{2}\right) \mathcal{E}^*\left(\omega' - \frac{\omega}{2}\right). \quad (3.5c)$$

The one-exciton Green function is

$$G(\omega, \mathbf{k}) = \frac{1}{\omega - \varepsilon(\mathbf{k}) + i\Sigma(\mathbf{k}) + i\Gamma(\mathbf{k})/2}. \quad (3.6)$$

$\Gamma(\mathbf{k})$ stands for the momentum-dependent exciton radiative and nonradiative decay rate which controls its lifetime [15]. In two dimensions, the radiative part of $\Gamma(\mathbf{k})$ has the form [16]

$$\Gamma(\mathbf{k}) = \frac{2\pi}{a^2} \frac{k_0^2 \mu^2 - (\mathbf{k} \cdot \boldsymbol{\mu}^\parallel)^2 - (k_0^2 - k^2) (\boldsymbol{\mu}^\perp)^2}{\sqrt{k_0^2 - k^2}} \theta(k_0 - k), \quad (3.7a)$$

$\varepsilon(\mathbf{k}) \equiv ck_0$, and $\theta(k_0 - k)$ is the Heaviside step function,

$$\theta(k_0 - k) = \begin{cases} 1; & k < k_0, \\ 0; & k > k_0. \end{cases} \quad (3.7b)$$

We have denoted the projection of the vector $\boldsymbol{\mu}$ parallel and normal to the lattice as $\boldsymbol{\mu}^\parallel$ and $\boldsymbol{\mu}^\perp$. Note that $\Gamma(\mathbf{k})$ is always positive.

The self-energy $\Sigma(\mathbf{k})$ represents the exciton lifetime due to inelastic scattering³⁾,

$$\Sigma(\mathbf{k}) = \frac{1}{2} \int f(\mathbf{p}, \mathbf{k}) d\mathbf{p} \quad (3.8a)$$

with the scattering kernel (see (3.11))

$$f(\mathbf{p}, \mathbf{p}') = 2\pi |V(\mathbf{p}', \mathbf{p}' - \mathbf{p})|^2 (1 + N[\Omega(\mathbf{p}' - \mathbf{p})]) \delta[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}') + \Omega(\mathbf{p}' - \mathbf{p})] + 2\pi |V(\mathbf{p}, \mathbf{p} - \mathbf{p}')|^2 N[\Omega(\mathbf{p} - \mathbf{p}')] \delta[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}') - \Omega(\mathbf{p} - \mathbf{p}')], \quad (3.8b)$$

and $N(\Omega)$ is the phonon occupation number,

$$N(\Omega) = [\exp(\Omega/kT) - 1]^{-1}. \quad (3.8c)$$

$\mathcal{G}_s^{(2)}$ is the two-exciton Green function calculated by assuming that excitons are free bosons; it can be expressed in terms of the vertex function $\bar{\Gamma}_s$ [8],

$$\begin{aligned} & \mathcal{G}_s^{(2)}(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) \\ &= G\left(\omega_0 + \frac{\omega}{2}, \mathbf{k}_0\right) G^*\left(\omega_0 - \frac{\omega}{2}, \mathbf{k}_0\right) G\left(\omega_s + \frac{\omega}{2}, \mathbf{k}_s\right) \\ & \quad \times G^*\left(\omega_s - \frac{\omega}{2}, \mathbf{k}_s\right) \bar{\Gamma}_s(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega). \end{aligned} \quad (3.9)$$

Here \mathbf{k}_0 is the projection of the incident field wave-vector on the system.

³⁾ We neglect the real parts of the self-energies $\Sigma(\mathbf{k})$ and $\Gamma(\mathbf{k})$.

Equations (3.5) and (3.9) constitute our final Green function expression for the time-dependent spectrum. Evaluating G and \bar{F}_s perturbatively in exciton–phonon coupling we obtain for the irreducible vertex \bar{F}_s

$$\bar{F}_s(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) = \int d\mathbf{p}' d\mathbf{p} g(\mathbf{p}', \mathbf{k}_0; \omega_0) \mathcal{D}(\mathbf{p}, \mathbf{p}'; \mathbf{q} = 0, \omega) g_s(\mathbf{k}_s, \mathbf{p}; \omega) \quad (3.10a)$$

with

$$g(\mathbf{p}, \mathbf{q}_0; \Omega) = 2\pi |V(\mathbf{q}_0, \mathbf{q}_0 - \mathbf{p})|^2 (1 + N[\Omega(\mathbf{q}_0 - \mathbf{p})]) \delta[\Omega - \varepsilon(\mathbf{p}) - \Omega(\mathbf{q}_0 - \mathbf{p})] \\ + 2\pi |V(\mathbf{p}, \mathbf{p} - \mathbf{q}_0)|^2 N[\Omega(\mathbf{p} - \mathbf{q}_0)] \delta[\Omega - \varepsilon(\mathbf{p}) + \Omega(\mathbf{p} - \mathbf{q}_0)], \quad (3.10b)$$

$$g_s(\mathbf{q}_s, \mathbf{p}; \Omega_s) = 2\pi |V(\mathbf{p}, \mathbf{p} - \mathbf{q}_s)|^2 (1 + N[\Omega_s(\mathbf{p} - \mathbf{q}_s)]) \delta[\Omega_s - \varepsilon(\mathbf{p}) + \Omega_s(\mathbf{p} - \mathbf{q}_s)] \\ + 2\pi |V(\mathbf{q}_s, \mathbf{q}_s - \mathbf{p})|^2 N[\Omega_s(\mathbf{q}_s - \mathbf{p})] \delta[\Omega_s - \varepsilon(\mathbf{p}) - \Omega_s(\mathbf{q}_s - \mathbf{p})]. \quad (3.10c)$$

The functions g and g_s can be interpreted as follows: $|G(\Omega, \mathbf{q}_0)|^2 g(\mathbf{p}, \mathbf{q}_0; \Omega)$ is the probability to absorb a photon with the frequency Ω and wave vector projection on the system \mathbf{q}_0 , creating an exciton with momentum \mathbf{p} , and creation or annihilation of a phonon to satisfy momentum conservation; $|G(\Omega_s, \mathbf{q}_s)|^2 g_s(\mathbf{q}_s, \mathbf{p}; \Omega_s)$ is a similar quantity which corresponds to an emission of photon with frequency Ω_s and wave-vector projection \mathbf{k}_s .

To clarify the physical significance of \mathcal{D} , let us consider the single-exciton density matrix in the momentum domain $n(\mathbf{p}, \mathbf{q}, t)$, which is defined as

$$n(\mathbf{p}, \mathbf{q}, t) \equiv \sum_m \langle \tilde{B}_m^\dagger \tilde{B}_n \rangle \exp \{ i[\mathbf{p} \cdot (\mathbf{R}_m - \mathbf{R}_n) + \frac{1}{2} \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{R}_n)] \}. \quad (3.11a)$$

This satisfies the Boltzmann equation [6]

$$\left\{ \frac{\partial}{\partial t} + i \left[\varepsilon \left(\mathbf{p} + \frac{\mathbf{q}}{2} \right) - \varepsilon \left(\mathbf{p} - \frac{\mathbf{q}}{2} \right) \right] \right\} n(\mathbf{p}, \mathbf{q}, t) \\ = - \int d\mathbf{p}'' [f(\mathbf{p}'', \mathbf{p}) n(\mathbf{p}, \mathbf{q}, t) - f(\mathbf{p}, \mathbf{p}'') n(\mathbf{p}'', \mathbf{q}, t)] - \Gamma(\mathbf{p}) n(\mathbf{p}, \mathbf{q}, t). \quad (3.11b)$$

\mathcal{D} is the Green function of the Boltzmann equation

$$n(\mathbf{p}, \mathbf{q}, t) = \int d\mathbf{p}' \mathcal{D}(\mathbf{p}, \mathbf{p}'; \mathbf{q}, t - t_0) n(\mathbf{p}', \mathbf{q}, t_0), \quad (3.11c)$$

where

$$\mathcal{D}(\mathbf{p}, \mathbf{p}'; \mathbf{q}t) \equiv \int \frac{d\omega}{2\pi} \exp(-i\omega t) \mathcal{D}(\mathbf{p}, \mathbf{p}'; \mathbf{q}\omega). \quad (3.11d)$$

Equations (3.5) to (3.10) describe the time-dependent luminescence spectra with exciton–phonon interactions. Equations (3.11) imply that the incident light creates exciton population in the exciton band, this population evolves due to exciton scattering by phonons following the Boltzmann equation, and the time-dependent spectrum reflects the evolution of the exciton population.

4. Time Resolved Luminescence from Disordered Aggregates

We next calculate the luminescence spectrum from a disordered molecular aggregate. The Hamiltonian now has the form [8]

$$\hat{H}_m(q) = \sum_n \Omega_n(q) \hat{B}_n^\dagger \hat{B}_n + \sum_{m \neq n} J_{mn} \hat{B}_m^\dagger \hat{B}_n + \hat{H}'(q), \quad (4.1)$$

where q represents a collection of additional coordinates which constitute static disorder. $\hat{H}'(q)$ is the Hamiltonian of these additional degrees of freedom, and their interactions with excitons are described by the q -dependence of the energies⁴⁾ $\Omega_n(q)$. We adopt a model of Gaussian diagonal disorder where the excitation energies Ω_n are distributed as follows:

$$\Omega_n = \Omega + U_n. \quad (4.2a)$$

The statistical properties of disorder are determined by the correlation function of U_n ,

$$\langle U_n \rangle_F = 0, \quad \langle U_m U_n \rangle_F = \sigma^2 \delta_{mn}, \quad (4.2b)$$

where the subscript F denotes an average over the static disorder.

As in the phonon case, the luminescence spectrum is given by (3.5), but with modified expressions for various Green functions. The one-exciton Green function $G(\omega, \mathbf{k})$ is given by [8]

$$G(\omega, \mathbf{k}) = \frac{1}{\omega - \varepsilon(\mathbf{k}) - \Sigma(\omega) + i\Gamma(\mathbf{k})/2}. \quad (4.3a)$$

The complex self-energy which is induced by disorder $\Sigma(\omega)$ satisfies the self-consistent equation [17, 8]

$$\Sigma(\omega) = \sigma^2 \int d\mathbf{k} \frac{1}{\omega - \varepsilon(\mathbf{k}) - \Sigma(\omega) + i\Gamma(\mathbf{k})/2}. \quad (4.3b)$$

$\bar{\Gamma}_s$ in this case has two contributions,

$$\bar{\Gamma}_s = \bar{\Gamma}_s^{(b)} + \bar{\Gamma}_s^{(c)}, \quad (4.4a)$$

with

$$\bar{\Gamma}_s^{(b)}(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) = \frac{i2\sigma^2 |\text{Im} \Sigma(\omega_0)|}{\omega + i\Gamma_0(\omega_0)} 2\pi \delta(\omega_s - \omega_0) \quad (4.4b)$$

and

$$\bar{\Gamma}_s^{(c)}(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) = \frac{2\sigma^2 |\text{Im} \Sigma(\omega_0)| i}{\omega + i\Gamma_0(\omega_0) + i(\mathbf{k}_0 + \mathbf{k}_s)^2 D(\omega_0)} 2\pi \delta(\omega_s - \omega_0). \quad (4.4c)$$

$\Gamma_0(\omega)$ is the frequency-dependent exciton inverse lifetime [8, 16],

$$\Gamma_0(\omega_0) \equiv \int d\mathbf{p} \Gamma(\mathbf{p}) |G(\mathbf{p}, \omega_0)|^2 \left\{ \int d\mathbf{p}' |G(\mathbf{p}', \omega_0)|^2 \right\}^{-1}, \quad (4.5a)$$

and the diffusion coefficient $D(\omega)$ is

$$D(\omega_0) \equiv \sigma^2 |\text{Im} \Sigma(\omega_0)| \int d\mathbf{p} \frac{\partial \varepsilon(\mathbf{p})}{\partial(\mathbf{p})} \frac{\partial \varepsilon(\mathbf{p})}{\partial(\mathbf{p})} |G(\mathbf{p}, \omega_0)|^4. \quad (4.5b)$$

It follows from (4.4) that the incoherent signal from a disordered aggregate has the same frequency as the incident light. The physical reason is that exciton scattering by static disorder is elastic and conserves the exciton energy. Therefore, the frequency-dispersed

⁴⁾ Off-diagonal disorder through the q dependence of J_{mn} is not considered here.

luminescence spectrum carries no information about exciton properties, and all the information is contained in the time resolved signal $S_{fl}(t, \mathbf{k}_s)$ [16],

$$S_{fl}(t, \mathbf{k}_s) \equiv \int \frac{d\omega}{2\pi} S_{fl}(\omega, t; \mathbf{k}_s). \quad (4.6)$$

Substituting (4.4a) into (3.5) and (3.9) we recast the incoherent signal in a form of two contributions with a very different angular dependence. $\bar{F}_s^{(b)}$ gives a homogeneous background and $\bar{F}_s^{(e)}$ is peaked in the direction opposite to the incident light ($\mathbf{k}_s = -\mathbf{k}_0$), which is the signature of backscattering [18].

5. The Luminescence Spectrum and Spectral Diffusion

Finally we consider a system with both static disorder and exciton–phonon interactions. Let us denote the elastic (disorder-induced) and inelastic (phonon-induced) exciton scattering rates by Γ_e and Γ_i respectively. When $\Gamma_e \approx \Gamma_i$, the signal can be calculated in the framework of Section 3 by simply modifying the functions f , g , and g_s . The situation is different in the other extreme when $\Gamma_e \gg \Gamma_i$. Though inelastic scattering is much weaker than elastic, one cannot neglect it since it leads to the relaxation of the exciton energy (spectral diffusion). The expression of Section 3 do not apply in this case since inelastic scattering is strongly affected by elastic processes. Fast elastic scattering leads to exciton transport in the energy space on the time scale longer than Γ_e^{-1} [8]. Elastic scattering creates a homogeneous exciton distribution $n(\mathbf{p})$ on the energy shell,

$$n(\mathbf{p}) = \int d\varepsilon n(\varepsilon) \delta(\varepsilon - \varepsilon(\mathbf{p})). \quad (5.1)$$

On the time scale $\sim \Gamma_e^{-1}$, inelastic scattering by phonons is responsible for exciton transport in energy space. The one-exciton Green function G still has the form of (4.3). The vertex \bar{F}_s can be represented in the form of (4.4a) with [8]

$$\bar{F}_s^{(b)}(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) = \sigma^4 \rho(\omega_s) \mathcal{D}(\omega_s, \omega_0; \omega), \quad (5.2a)$$

$$\begin{aligned} \bar{F}_s^{(e)}(\omega_0 \mathbf{k}_0, \omega_s \mathbf{k}_s; \omega) \\ = \frac{i2\sigma^2 |\text{Im} \Sigma(\omega_0)|}{\omega + i\Gamma_0(\omega_0) + i\Gamma_{ph}(\omega_0) + i(\mathbf{k}_0 + \mathbf{k}_s)^2 D(\omega_0)} 2\pi \delta(\omega_s - \omega_0). \end{aligned} \quad (5.2b)$$

In (5.2b) $\rho(\omega_s)$ is the exciton density of states,

$$\rho(\omega_s) = -2 \text{Im} \int d\mathbf{p} G(\omega_s, \mathbf{p}). \quad (5.3)$$

$\Gamma_{ph}(\omega_0)$ is the decay rate of exciton population at the energy ω_0 of the incident light due to exciton–phonon scattering,

$$\Gamma_{ph}(\omega) = \int \frac{d\varepsilon}{2\pi} \rho(\varepsilon) F(\varepsilon, \omega), \quad (5.4)$$

$n(\varepsilon)$ satisfies the master equation

$$\frac{\partial n(\varepsilon)}{\partial t} = \int \frac{d\varepsilon'}{2\pi} \rho(\varepsilon') [F(\varepsilon, \varepsilon') n(\varepsilon') - F(\varepsilon', \varepsilon) n(\varepsilon)] - \Gamma_0(\varepsilon) n(\varepsilon) \quad (5.5a)$$

and \mathcal{D} is the Green function of the energy transport equation,

$$n(\varepsilon, t) = \int \frac{d\varepsilon'}{2\pi} \rho(\varepsilon') \mathcal{D}(\varepsilon, \varepsilon'; t) n(\varepsilon', 0). \quad (5.5b)$$

The kernel $F(\varepsilon, \varepsilon')$ represents exciton transport in energy space, i.e., $F(\varepsilon, \varepsilon')$ is the probability for an exciton to be scattered from energy ε' to ε ,

$$\begin{aligned} F(\varepsilon, \varepsilon') = & 2\pi\sigma^4 \int d\mathbf{k} d\mathbf{k}' |G(\varepsilon, \mathbf{k})|^2 |G(\varepsilon', \mathbf{k}')|^2 \\ & \times \{ |V(\mathbf{k}', \mathbf{k}' - \mathbf{k})|^2 (1 + N(\varepsilon' - \varepsilon)) \delta(\varepsilon - \varepsilon' + \Omega(\mathbf{k}' - \mathbf{k})) \\ & + |V(\mathbf{k}, \mathbf{k} - \mathbf{k}')|^2 N(\varepsilon - \varepsilon') \delta(\varepsilon - \varepsilon' - \Omega(\mathbf{k} - \mathbf{k}')) \}. \end{aligned} \quad (5.6)$$

The contribution related to $\bar{F}_s^{(c)}$ (5.2b) describes backscattering, the signal has the same frequency of the incident light and decays on the time scale of Γ_i^{-1} due to the term $\Gamma_{\text{ph}}(\omega_0)$ in the denominator. Physically this means that backscattering is connected with the phase memory [18] which is destroyed by inelastic processes. The contribution related to $\bar{F}_s^{(b)}$ (5.2a) forms a homogeneous angular distribution, and the time-dependent spectrum reflects spectral diffusion due to exciton transport in the energy domain.

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