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Line shapes and transport for excitons with stochastic coupling[a)]

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The effect of nonlocal fluctuations on the line shape and dynamics of exciton states is considered, using a stochastic perturbation approach. The cumulant expansion is truncated at second order. The usual Gaussian and motional narrowing limits are treated and the limitations of the model are discussed.

I. INTRODUCTION

The Haken–Strobl model[1] of excitation line shapes and energy transfer in molecular aggregates has been extremely useful for interpreting the experimental results in such systems. The simplicity of this model lies in the assumption that the bath variables (with which the excitation interacts) relax extremely quickly compared to the rate of relaxation of the excitation. The relevant correlation functions of bath variables are then replaced by a delta function in time. This allows an exact solution of the equations of motion of the excitation to be found. Recently, Sumi[2] and Blumen and Silbey[3] have relaxed this assumption and assumed that the correlation function for *local* fluctuations decays on a time scale γ^{-1}; this allows a broader range of behavior for the line shape and dynamics. However, these authors did not look at the *nonlocal* fluctuations and their effect on the properties of the system. In the present note, we examine the easing of the restriction of a delta function correlation in time for *both* local and nonlocal fluctuations. We treat both the dimer and the crystal. In Sec. II, we discuss the Hamiltonian and assumptions of the model. In Secs. III and IV, we calculate the optical line shape and discuss exciton dynamics of a pure crystal. In Sec. V, the line shape and dynamics of a dimer embedded in a host crystal are determined, and in Sec. VI, we conclude with a discussion of the limitations of the model.

II. THE HAMILTONIAN

A Hamiltonian containing excitation–phonon coupling is

$$\mathcal{H}=\sum_n \epsilon_n a_n^\dagger a_n+\sum_{n,m} J_{nm} a_n^\dagger a_m \ , \tag{2.1}$$

where $a_n^\dagger(a_n)$ create (destroy) an excitation on site n, ϵ_n is the local site energy, and J_{nm} is the transfer integral from site n to site m. We can separate the average or nonfluctuating part of $\mathcal{H}$ as $\mathcal{H}_0$ and treat the remainder as a perturbation:

$$\begin{aligned}\mathcal{H}_0&=\sum_n \epsilon a_n^\dagger a_n+\sum_{n,m} J_{nm} a_n^\dagger a_m \ ,\\ V&=\sum_n \delta\epsilon_n a_n^\dagger a_n+\sum_{n,m}\delta J_{nm} a_n^\dagger a_m \ .\end{aligned} \tag{2.2}$$

The terms $\delta\epsilon_n$ and δJ_{nm} are complicated functions of the phonon variables; in the interaction representation with respect to the phonon Hamiltonian (not explicitly written), these terms will be time dependent. We therefore assume as the fundamental Hamiltonian for our system $\mathcal{H}=\mathcal{H}_0+V$, where $\delta\epsilon_n$ and δJ_{nm} are replaced by time-dependent functions. The term $\delta\epsilon_n(t)$ represents a *local* fluctuation of the site energy, and $\delta J_{nm}(t)$ represents a *nonlocal* fluctuation of the transfer integral. We assume, along with Haken and Strobl,[1] that the fluctuations are a Gaussian–Markov process[4] with zero average:

$$\langle\delta\epsilon_n(t)\rangle=0=\langle\delta J_{nm}(t)\rangle \ . \tag{2.3}$$

In contrast to Haken and Strobl,[1] we assume[2,3]

$$\langle\delta\epsilon_n(t)\delta\epsilon_m(0)\rangle=\delta_{nm}D^2\, e^{-\eta|t|}$$

and (2.4)

$$\langle\delta J_{nm}(t)\delta J_{n'm'}(0)\rangle=(\delta_{nn'}\delta_{mm'}+\delta_{nm'}\delta_{n'm})A^2(n-m)\, e^{-\alpha|t|} \ .$$

We have used a one-dimensional notation; however, each index n can be thought of as a set of d numbers for d-dimensional problems. The form $A^2(n-m)$ means that A^2 depends on the distance between sites n and m. In the following, we will often assume only nearest neighbor correlations [$A^2(n-m)=0$ for further neighbors], but this restriction is easily lifted.

In the limit that A^2, D^2, η, and $\alpha\to\infty$ such that $D^2/\eta\to\gamma_0$ and $A^2(n-m)/\alpha\to\gamma(n-m)$, the Haken–Strobl model is recovered. Since D and A are measures of the strength of the exciton–phonon interaction and η and α are measures of the relaxation rate of the fluctuations, the Haken–Strobl assumptions refer to rapidly relaxing strong coupling (corresponding to a motionally narrowed limiting case).

The method of solution for the line shape and density matrix of the excitation is the same as before[3]: we compute the equations of motion for the density matrix or Green's function in the second cumulant approximation. Note that since we have assumed that the fluctuations are a Gaussian–Markov process, we might think that the result up to the second cumulant is exact; however, since we are dealing with an operator equation with noncommuting operators,[5] higher cumulants are nonzero, in contrast to a statement made by Blumen and Silbey.[3]

III. LINE SHAPES

Following the method of the earlier paper,[3] we write the line shape as

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$$I(\omega)=\sum_k |\mu_k|^2 \frac{\mathrm{Re}}{\pi}\int_0^\infty dt\, e^{i\omega t}\langle 0|\langle a_k(t)\rangle a_k^\dagger|0\rangle\ , \tag{3.1}$$

where $|0\rangle$ is the ground electronic state of the system. The dipole moment μ_k is nonzero only near $k=0$ in the exciton system, so that only that term survives the sum in Eq. (3.1).

The time dependence of $a_k(t)$ is

$$\frac{d}{dt}a_k(t)=i\mathcal{H}^x(t)a_k(t)\equiv i[\mathcal{H}(t),\, a_k(t)]\ , \tag{3.2}$$

or, in the interaction representation,

$$\tilde{a}_k(t)\equiv e^{-i\mathcal{H}_0 t}a_k(t)\, e^{i\mathcal{H}_0 t}\ , \tag{3.3}$$

$$\frac{d}{dt}\tilde{a}_k(t)=+i\tilde{V}^x(t)\tilde{a}_k(t)\ . \tag{3.4}$$

The solution to this equation is

$$\langle\tilde{a}_k(t)\rangle=\left\langle \exp_T\left[+i\int_0^t d\tau\,\tilde{V}^x(\tau)\right]\right\rangle a_k(0)\ . \tag{3.5}$$

We can express the time-ordered exponential using a Kubo cumulant expansion[6] to find in second order

$$\frac{d}{dt}\langle\tilde{a}_k(t)\rangle=\tilde{\kappa}_2(t)\langle\tilde{a}_k(t)\rangle\ , \tag{3.6}$$

where

$$\tilde{\kappa}_2(t)=-\int_0^t d\tau_1\int_0^{\tau_1} d\tau_2\,\langle\tilde{V}^x(\tau_1)\tilde{V}^x(\tau_2)\rangle\ , \tag{3.7}$$

and the first cumulant is zero by Eq. (2.3). In Sec. VI, we will discuss the limitations imposed on our model by ignoring cumulants of higher order. Using Eqs. (2.2) and (2.4) to compute $\tilde{\kappa}_2(t)$, and putting this into Eq. (3.1), we find

$$I(\omega)=\sum_k |\mu_k|^2\frac{\mathrm{Re}}{\pi}\int_0^\infty dt\exp[i(\omega-E_k)t]\, e^{-\phi_k(t)}\ , \tag{3.8}$$

where

$$\phi_k(t)=\int_0^t d\tau\int_0^\tau d\tau_1\left[D^2 e^{-\pi\tau_1}g_k(\tau_1)+2A^2 e^{-\alpha\tau_1}g_k(\tau_1)\right.$$
$$\left.+2A^2 e^{-\alpha\tau_1}N^{-1}\sum_{k_1}\exp[i(E_k-E_{k_1})\tau_1]\cos(k+k_1)\right]\ , \tag{3.9}$$

$$g_k(\tau)=N^{-1}\sum_{k_1}\exp[i(E_k-E_{k_1})\tau]\ . \tag{3.10}$$

By using the exciton density of states $g(\omega)$, we can express $g_k(\tau)$ as

$$g_k(\tau)=e^{iE_k\tau}\int d\omega\, g(\omega)\, e^{-i\omega\tau}\ . \tag{3.11}$$

To compute the optical line shape of the crystal, we use two forms of $g(\omega)$:

$$g^{\mathcal{K}}(\omega)=\begin{cases}(2/\pi B^2)[B^2-(\omega-E_m)^2]^{1/2}, & |\omega-E_m|\le B\ ,\\ 0\ , & |\omega-E_m|>B\ ,\end{cases} \tag{3.12a}$$

$$g^L(\omega)=\frac{(B/\pi)}{(\omega-E_m)^2+B^2}\ , \tag{3.12b}$$

where the exciton band has been assumed to be symmetric about the mean energy E_m (*henceforth taken to be zero, for notational simplicity*) and of width $2B$. The resulting $I(\omega)$ is rather complicated; however, we may evaluate the results for various orderings of parameters as was done by Blumen and Silbey[3] for local correlations alone. We will comment only on the effects of nonlocal fluctuations here.

In the limit of large fluctuations ($D\gg B,\eta$ and/or $A\gg B,\alpha$), the line shape is Gaussian of width $2(D^2+2A^2)^{1/2}(2\ln 2)^{1/2}$, independent of the exciton density of states.

In the opposite limit of motional narrowing, where $D\ll B$, or η and $A\ll B$ or α, the absorption line shape is Lorentzian. In order to calculate the widths and shifts, we use Eqs. (3.8)–(3.10), rewriting Eq. (3.9) as

$$\phi_k(t)=D^2\int_0^t d\tau\int_0^\tau d\tau_1\, e^{-\pi\tau_1}g_k(\tau_1)$$
$$+2A^2\int_0^t d\tau\int_0^\tau d\tau_1 f_k(\tau_1)\, e^{-\alpha\tau_1}\ , \tag{3.13}$$

where

$$f_k(\tau_1)=g_k(\tau_1)$$
$$+N^{-1}\sum_{k_1}\exp[i(E_k-E_{k_1})\tau_1]\cos(k+k_1)\ . \tag{3.14}$$

Since $\mu_k=0$ except for $k\approx 0$, we have to evaluate only ϕ_0. In order to present analytic results, we use the approximation that $\cos k_1\cong E_{k_1}/B$. Then, using the density of states $g(\omega)$,

$$f_0(\tau)=g_0(\tau)+e^{iE_0 t}\int d\omega\, g(\omega)\, e^{-i\omega t}\omega/B\ . \tag{3.15}$$

For a Lorentzian density of states,

$$g_0(\tau)=e^{iE_k\tau}e^{-B|\tau|}\ , \tag{3.16}$$

$$f_0(\tau)=(1-i)g_0(\tau)\ . \tag{3.17}$$

For a hemicircular density of states,

$$g_0(\tau)=2\, e^{iE_0\tau}\frac{J_1(B\tau)}{B\tau}\ , \tag{3.18}$$

$$f_0(\tau)=2\, e^{iE_0\tau}\frac{[J_1(B\tau)-iJ_2(B\tau)]}{B\tau}\ . \tag{3.19}$$

Using these forms in the limit $D\ll B$, η and $A\ll B$, α, we find for a Lorentzian density of exciton states the usual Lorentzian line shape with shift Γ_2 and width Γ_1:

$$\Gamma_1^L=\frac{D^2(B+\eta)}{(B+\eta)^2+E_0^2}+\frac{2A^2(B+\alpha+E_0)}{(B+\alpha)^2+E_0^2}\ , \tag{3.20}$$

$$\Gamma_2^L=\frac{D^2E_0}{(B+\eta)^2+E_0^2}+\frac{2A^2(E_0-\alpha-B)}{(B+\alpha)^2+E_0^2}\ . \tag{3.21}$$

In the case of a hemicircular density of states, the forms for Γ_1 and Γ_2 are much more complicated; however, in the limit $D\ll B$, η and $A\ll B$, α, they reduce to the same form as those of the Lorentzian density of states, i.e.,

$$\Gamma_1=(D^2/\eta)+(2A^2/\alpha)\ ,$$
$$\Gamma_2=(D^2E_0/\eta^2)-(2A^2/\alpha)\ ,\quad \alpha,\eta\gg B \tag{3.22}$$

(rapid bath modulation), and

$$\Gamma_1 = (D^2/2B) + (2A^2/B) ,$$

$$\Gamma_2 = (D^2/2B) - (A^2\alpha/B^2) , \quad B \gg \eta, \alpha \tag{3.23}$$

(rapid exciton transfer). In the above we have assumed $E_0 = B$ (i.e., the $k=0$ exciton level is at the top of the band).

IV. DYNAMICS

Exciton transport is described by the reduced density matrix $\sigma(t)$, which is the average of $\rho(t)$, the full crystal density matrix, over the canonical phonon ensemble. By the same procedure outlined above for $\langle \tilde{\alpha}_k(t) \rangle$ we find

$$\frac{d}{dt}\langle \tilde{\rho}(t) \rangle = \frac{d}{dt}\tilde{\sigma}(t) = + \dot{\tilde{\kappa}}_2(t)\tilde{\sigma}(t) . \tag{4.1}$$

By calculating a diagonal matrix element of Eq. (4.1) in momentum space, we arrive at the general equation of motion:

$$\dot{\tilde{\sigma}}_{kk}(t) = -\tilde{\sigma}_{kk}(t)\int_0^t d\tau \left\{ 2D^2 e^{-\eta\tau}\,\mathrm{Re} g_k(\tau) + 4A^2 e^{-\alpha\tau}\,\mathrm{Re} g_k(\tau) + 4A^2 e^{-\alpha\tau}\frac{\mathrm{Re}}{N}\sum_{k_1}\exp[i(E_k - E_{k_1})\tau]\cos(k+k_1)\right\}$$
$$+ \sum_{k_1}\tilde{\sigma}_{k_1k_1}(t)\int_0^t d\tau\left[\frac{2}{N}(D^2 e^{-\eta\tau} + 2A^2 e^{-\alpha\tau})\cos(E_k - E_{k_1})\tau + \frac{4A^2}{N}e^{-\alpha\tau}\cos(k+k_1)\cos(E_k - E_{k_1})\tau\right] . \tag{4.2}$$

In a crystal we can describe excitation transfer in terms of its diffusion coefficient. It has been shown[7,8] that the diffusion coefficient of an exciton may be expressed approximately in terms of its momentum-space representation as

$$D = \sum_k \sigma_{kk}^{eq}\left(\frac{V_k^2}{\Gamma_{kk}} + \gamma_{kk}\right) , \tag{4.3}$$

where $V_k = \nabla_k E_k$ is the exciton velocity. γ_{kk}, which can be interpreted as a hopping term,[8] is given by

$$\gamma_{kk} = -\mathrm{Re}\left[\sum_q \frac{\partial^2 W_{q,q+\lambda;k,k+\lambda}}{\partial\lambda^2}\right]_{\lambda=0} + \frac{\partial^2\Gamma_{kk}}{\partial k^2} , \tag{4.4}$$

where

$$W_{kk';qs} = \int_0^\infty d\tau \{\langle V_{sk'}V_{kq}(\tau)\rangle \exp[i(E_s - E_{k'})\tau] + \langle V_{sk'}(\tau)V_{kq}\rangle \exp[i(E_k - E_q)\tau]\} \tag{4.5}$$

and

$$\Gamma_{kk} = \sum_q W_{qq;kk} . \tag{4.6}$$

For our model

$$\gamma_{kk} = \mathrm{Re}\sum_q \frac{1}{N}\left[4A^2[\cos(k+q)+1]\frac{\alpha}{\alpha^2 + (E_k - E_q)^2}\right.$$
$$- 4A^2\sin(\lambda+q)(V_k - V_q)\frac{2\alpha(E_k - E_q)}{[\alpha^2 + (E_k - E_q)^2]^2} + \frac{\partial^2}{\partial\lambda^2}(E_{k+\lambda} - E_{q+\lambda})_{\lambda=0}\left\{\frac{2D^2\eta(E_k - E_q)}{[\eta^2 + (E_k - E_q)^2]^2} + \frac{4A^2\eta(E_k - E_q)}{[\eta^2 + (E_k - E_q)^2]^2}[1 + \cos(k+q)]\right\}$$
$$\left. + (V_k - V_q)^2\left(\frac{8D^2\eta^3}{[\eta^2 + (E_k - E_q)^2]^3} - \frac{6D^2\eta}{[\eta^2 + (E_k - E_q)^2]^2} + \left\{\frac{16A^2\eta^3}{[\eta^2 + (E_k - E_q)^2]^3} - \frac{12A^2\eta}{[\eta^2 + (E_k - E_q)^2]^2}\right\}[1 + \cos(k+q)]\right)\right] . \tag{4.7}$$

Γ_{kk} is the scattering rate out of state k and is given by the first term in braces in Eq. (4.2). Using Lorentzian and hemicircular densities of exciton states to calculate $g_k(\tau)$, we find

$$\Gamma_{kk}^L = [2D^2/(\eta + B)] + [4A^2/(\alpha + B)]$$

and (4.8)

$$\Gamma_{kk}^H = (4D^2/B^2)(\sqrt{\eta^2 + B^2} - \eta) + (8A^2/B^2)(\sqrt{\alpha^2 + B^2} - \alpha) .$$

We see that the scattering rate out of a k state is inversely proportional to either the exciton or phonon bandwidth, whichever is larger.

These results are easily compared to those of the Haken and Strobl[1] model, which is valid in the limit of rapid bath modulation. For the case ($\eta \gg B$, $D;\alpha \gg B, A$), Γ_{kk} and γ_{kk} reduce to

$$\Gamma_{kk}^H = \Gamma_{kk}^L = (2D^2/\eta) + (4A^2/\alpha)$$

and (4.9)

$$\gamma_{kk} = 4A^2/\alpha .$$

In terms of Haken and Strobl's parameters $(D^2/\eta) = \gamma_0$ and $(A^2/\alpha) = \gamma_1$, we have

$$\Gamma_{kk} = 2\gamma_0 + 4\gamma_1 ,$$

$$\gamma_{kk} = 4\gamma_1 . \tag{4.10}$$

These are exactly the results found by Munn and Silbey[8] when applying the Haken and Strobl model to Eqs. (4.4)–(4.6).

In the limit that $A^2 \to 0$, our results for line shapes and dynamics reduce to those of Blumen and Silbey.[3]

V. THE DIMER

For the case of a dimer embedded in a host crystal, we can perform the summations $g_k(\tau)$ and $f_k(\tau)$ exactly. The equations describing the line shape and $\dot{\sigma}(t)$ of a symmetric dimer are the same as those used for the crystal, but with the A^2 terms reduced by a factor of $\frac{1}{2}$ (these equations were derived assuming that each crystal site had two sites adjacent to it). We designate the two dimer states in momentum space as $\kappa = 0$ and $\kappa = \pi$ (in units of $1/a$, where a is the lattice spacing), with energies at the top and bottom of the exciton band, respectively. The dimer bandwidth is set equal to B (half that of the crystal) with the zero of energy chosen to be at the top of the band for simplicity.

Equation (3.6) for the dimer is

$$\frac{d}{dt}\langle a_k(t)\rangle = -\int_0^t d\tau\left[\frac{D^2}{2}e^{-\eta\tau}(1+e^{iB\tau})+A^2e^{-\alpha\tau}\right]\langle a_k(t)\rangle\ , \tag{5.1}$$

which, when solved for $\langle a_k(t)\rangle$ and Fourier transformed, results in a fairly complicated expression. However, by using a projection operator technique[9] to second order to derive Eq. (5.1), we get a convolution

$$\frac{d}{dt}\langle a_k(t)\rangle = -\int_0^t d\tau\left[\frac{D^2}{2}\exp(-\eta\,|t-\tau|)\right.$$
$$\left.\times(1+\exp[iB(t-\tau)])+A^2\exp(-\alpha\,|t-\tau|)\right]\langle a_k(\tau)\rangle\ , \tag{5.2}$$

which is easily Fourier transformed to yield the following line shape:

$$I(\omega) = \frac{(|\mu_0|^2/\pi)\Gamma_1(\omega)}{\Gamma_1^2(\omega)+[\omega-\Gamma_2(\omega)]^2}\ ,$$
$$\Gamma_1(\omega) = \frac{D^2}{2}\left[\frac{\eta}{\eta^2+\omega^2}+\frac{\eta}{\eta^2+(\omega+B)^2}\right]+\frac{A^2\alpha}{\alpha^2+\omega^2}\ , \tag{5.3}$$
$$\Gamma_2(\omega) = \frac{D^2}{2}\left[\frac{\omega}{\eta^2+\omega^2}+\frac{\omega+B}{\eta^2+(\omega+B)^2}\right]+\frac{A^2\omega}{\alpha^2+\omega^2}\ .$$

In the motional narrowing region, where D is small compared to η and/or B, we have a sharp Lorentzian peak centered near $\omega = 0$ due to absorption in the $\kappa = 0$ state. The width and shift in this case are

$$\Gamma_1 \approx \frac{D^2}{2\eta}+\frac{D^2\eta}{2(\eta^2+B^2)}+\frac{A^2}{\alpha}\ ,$$
$$\Gamma_2 \approx \frac{D^2B}{2(\eta^2+B^2)}\ .$$

The transition rate between the two dimer states is proportional to the square of the local fluctuation amplitude, as will be shown below. Consequently, as D^2 becomes larger, a peak develops near $\omega = B$, due to the $\kappa = \pi$ state. These peaks become broader as D increases, and shift away from each other.

Equation (4.2) for the dimer is found to be

$$\frac{d\tilde{\sigma}_{11}(t)}{dt} = [\tilde{\sigma}_{22}(t)-\tilde{\sigma}_{11}(t)]$$
$$\times\left[\frac{D^2\eta}{\eta^2+B^2}+\frac{D^2e^{-\eta t}}{\eta^2+B^2}(B\sin Bt-\eta\cos Bt)\right]. \tag{5.4}$$

If we include the other possible correlations $\langle\delta\epsilon_1(t)\delta\epsilon_2(0)\rangle$ and $\langle\delta\epsilon_1(t)\delta J(0)\rangle$, which may be important at low temperatures, we find that only the first gives a contribution. Therefore, within the limits of our approximation, the transfer of energy in a dimer depends only upon local correlations. Redfield's reduced density matrix formalism,[10,11] which utilizes a second-order perturbation expansion, reproduces these results.

VI. LIMITATIONS

As stated earlier, the spectrum of systems to which our model can be applied is limited by the second cumulant approximation. In a recent paper addressing this problem, Rips and Čápek[12] show that the operators $V(t_1)$ and $V(t_2)$ commute in the limits of vanishing exciton bandwidth or very fast thermal modulation, i.e., the second cumulant approximation is exact for the case of no exciton motion (Anderson–Kubo model) or a delta-function correlation time (Haken and Strobl model).

For what orderings of parameters then is our approximation a suitable one? For $\eta \gg B, D$ one can show that the local contributions from the second- and fourth-order cumulants are proportional to D^2/η and D^4/η^3, respectively. Therefore, the correction terms in the region of rapid vibrational modulation are negligibly small. For narrowing by excitation transfer ($B \gg \eta, D$) the contributions from these two cumulants are proportional to D^2/B and D^4/B^3, respectively, and the second cumulant approximation is again a good one. In general, our model is quite valid in the entire motional narrowing region where $D^2 \ll B^2+\eta^2$, and in the narrow exciton bandwidth region where $D^2B^2 \ll \eta^4$.

The nonlocal contributions from higher-order cumulants will exhibit the same behavior, i.e., higher-order corrections are negligible when $A^2 \ll B^2+\alpha^2$. This relation will, in general, always be satisfied, since A is a measure of the fluctuation in J_1, which is a fraction of the bandwidth B. Therefore, our model should be quite accurate with respect to calculating nonlocal contributions to the line shapes and dynamics.

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