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Exciton line shapes and migration with stochastic exciton lattice coupling[a)]

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In a recent article, Sumi [J. Chem. Phys. 67, 2943 (1977)] has discussed the optical line shape of an exciton interacting with phonons using a Gaussian Markov process for this interaction. By assuming that the correlation time of the process is nonzero, he was able to explore various limits of (motional) narrowing of the line. His analysis used a dynamic coherent potential approximation (CPA) in order to calculate the line shape. In the present paper, we derive these results in closed analytic form, without the CPA, by using standard analysis. Since our results agree with Sumi very closely, the present approach provides a simple way of understanding the underlying physics. In addition, we show how the exciton density of states enters in a simple way, and compare the hemicircular and the Lorentzian forms for this density of states.

I. INTRODUCTION

One of the most readily available means of gaining experimental evidence about the microscopic interactions in a system consists in analyzing its optical line shape.[1] However, since the information that line shapes provide is not very detailed, it is important to be able to interpret it in terms of theoretical models that are realistic, i.e., include other available information about the system. Thus, one is led to consider moderately complex models; these models should not be too simple since they must be able to mimic the behavior of the investigated materials; nor should they be complex, since one must be able to determine unambiguously for each particular substance, from the calculated and the measured line shapes, the parameters of the model.

A physical problem in which the study of the optical line shapes has received much attention and proven to be particularly fruitful is the exciton problem. Excitons in molecular crystals have been investigated extensively by light absorption.[2] Since their properties, depending on the material and on the experimentally imposed conditions, vary widely, one obtained classes of excitonic line shapes that show considerable differences.

A classical phenomenologic approach to the excitonic line shape is due to Haken and Strobl.[3] In their case, the Hamiltonian is assumed to have the form

$$H=\sum_k E_k a_k^+ a_k + \sum_{n,m} V_{nm}(t)\, a_n^+ a_m \; . \qquad (1.1)$$

Here, a_k^+ and a_k are the creation and annihilation operators of an exciton with momentum k and energy E_k, respectively, while a_n^+ and a_n correspond to the exciton localized at the nth site of the lattice. The terms $V_{nm}(t)$ represent stochastic fluctuations in the energy $(n=m)$ and interaction $(n\neq m)$ of localized excitons. These fluctuations are due to the scattering of the excitons by lattice vibrations.

Haken and Strobl's assumption about $V_{nm}(t)$ is that

$$\langle V_{nm}(t)\rangle = 0 \qquad (1.2)$$

and that

$$\langle V_{nm}(t) V_{n'm'}(t')\rangle = \Gamma_{|n-m|}\,\delta(t-t')[\delta_{nn'}\delta_{mm'} + \delta_{nm'}\delta_{n'm}(1-\delta_{nn'})] \, . \qquad (1.3)$$

$\langle\;\rangle$ denotes the statistical ensemble average. Relation (1.3) implies that fluctuations at different times are uncorrelated and corresponds to the shortest correlation time limit of a Gaussian–Markov process. It relies on the assumption that the phase randomization of the normal mode lattice components is very fast compared to the exciton dynamics.

Sumi's approach[1] following Toyozawa[4] consists of relaxing this constraint; he assumes that the time dependence of Eq. (1.3) is given by an exponentially decaying function, i.e., is a Gaussian Markov process with a specified rate $\gamma = 1/\tau_0$. Since this renders the problem more complex, one is led to consider first only the fluctuations in site energy and to set

$$\langle V_{nn}(t) V_{mm}(t')\rangle = D^2 \exp(-\gamma|t-t'|)\delta_{nm} \, . \qquad (1.4)$$

It is this Hamiltonian that we will consider in the following. Note that γ will be a measure of the phonon bandwidth or dispersion.

What remains to complete the characterization of the Hamiltonian (1.1) is now only to specify E_k as the function of k, i.e., the excitonic density of states. To simulate the density of states, one may use different shapes, the most usual being Lorentzians, Gaussians, or the hemicircular shapes of Hubbard.[5] It is the last one that Sumi used in determining by an iterative numerical method the line shape of Eq. (1.1) in the context of his dynamical coherent potential approximation.

In this paper, we show that many results for the line shape may be obtained analytically for the excitonic densities of state mentioned above (including the hemicircular form), by making use of a Kubo-type cumulant

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expansion.[6-8] We recover the results of Ref. 1 for both the fast and the slow modulation limit; they follow indeed only from the assumed form of the Hamiltonian and are not due to the dynamical coherent potential approximation used by Sumi.[1]

The paper is structured as follows: In Sec. II, we give the formula for the line shape and present the master equation that the exciton density matrix obeys. In Sec. III, we evaluate the line shape formula for different densities of state and present the explicit analytic solutions obtained; we also provide a comparison to the numerical results of Sumi.[1] In Sec. IV, we discuss the coherent *versus* incoherent exciton motion for different parameters of the model. Our summary and conclusions are found in Sec. V.

II. THE LINE SHAPE

The generalized cumulant expansion of Kubo[6] is a particularly suitable procedure for deriving line shape formulas when the fluctuating potentials are Gaussian random processes, since a local time description results. The general formula for the line shape $I(\omega)$ is[9]

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^{+\infty} dt\, e^{i\omega t}\langle 0|\langle\hat{\mu}(t)\rangle\hat{\mu}(0)|0\rangle\ , \tag{2.1}$$

where $|0\rangle$ is the ground state of the system and we have assumed that the exciton energy is much larger than k_BT. Also, we have averaged over the lattice fluctuations: $\langle\hat{\mu}(t)\rangle$ is the average over the lattice fluctuations of $\hat{\mu}(t)$, where $\hat{\mu}(t)$ is the dipole moment operator in the Heisenberg representation. The dipole moment operator ator can be written as

$$\mu=\sum_n \mu_n(a_n+a_n^+)=\sum_k \mu_{-k}(a_k^+ + a_{-k}) \tag{2.2}$$

so that

$$I(\omega)=\sum_k |\mu_k|^2\frac{\operatorname{Re}}{\pi}\int_0^{+\infty} dt\, e^{i\omega t}\langle 0|\langle a_k(t)\rangle a_k^+|0\rangle$$
$$\equiv\sum_k |\mu_k|^2 I_k(\omega)\ . \tag{2.3}$$

For excitons, μ_k is nonzero only for $k\approx 0$ [actually $k\approx 10^{-3}(\pi/a)$, where a is a lattice distance].

The time dependence of $\langle a_k(t)\rangle$ may be found from the Heisenberg equations of motion [$H(t)$ is defined in Eq. (1.1)]

$$\frac{d}{dt}a_k(t)=i[H(t),\,a_k(t)]\equiv iH^X(t)\,a_k(t)\ , \tag{2.4}$$

where the superscript X is defined by Eq. (2.4). By transforming to the interaction representation and assuming that $V_{nn}(t)$ is a Gaussian–Markov process obeying Eqs. (1.2) and (1.4), we find in Appendix A that

$$I_k(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^{\infty} d\tau\, e^{i(\omega-E_k)\tau}\times\exp\left[-D^2\int_0^{\tau}d\tau_1\int_0^{\tau_1}d\tau_2\, e^{-\gamma\tau_2}g_k(\tau_2)\right]\ , \tag{2.5}$$

where

$$g_k(\tau)=\frac{1}{N}\sum_{k_1} e^{-i(E_{k_1}-E_k)\tau}=e^{iE_k\tau}\int d\omega\, g(\omega)\, e^{-i\omega\tau} \tag{2.6}$$

and $g(\omega)$ is the normalized density of exciton states. These are the formulas we will use to calculate the line shape.

In order to discuss exciton diffusion, we will need the equation of motion of the exciton density matrix.[10,11] The full density matrix of the system obeys the equation

$$\dot{\rho}(t)=-iH^X(t)\,\rho(t) \tag{2.7}$$

and we want the equation of motion of the exciton density matrix $\sigma(t)$:

$$\sigma(t)\equiv\langle\rho(t)\rangle\ . \tag{2.8}$$

Using the fact that $V(t)$ is a Gaussian–Markov process (see Appendix B) and transforming $\sigma(t)$ to the interaction representation $\tilde{\sigma}(t)$ as

$$\tilde{\sigma}(t)=e^{iH_0^X t}\,\sigma(t)\ , \tag{2.9}$$

we find for the diagonal elements

$$\frac{d}{dt}\tilde{\sigma}_{kk}=-\tilde{\sigma}_{kk}(t)\left[\operatorname{Re}\int_0^t d\tau\, 2D^2e^{-\gamma\tau}g_k(\tau)\right]+\frac{1}{N}\sum_{k_1}\tilde{\sigma}_{k_1k_1}(t)\left[\int_0^t d\tau\, 2D^2e^{-\gamma\tau}\cos(E_k-E_{k_1})\tau\right]\ , \tag{2.10}$$

where Re means real part. Note that the multiplying factor of $\tilde{\sigma}_{kk}$ in Eq. (2.10) is related to the exponent in Eq. (2.5).

III. EXCITON DENSITIES OF STATES AND OPTICAL LINE SHAPES

A. Densities of states

In the previous section, we pointed out that the exciton density of states $g(\omega)$ enters the line shape formula (2.5) through $g_k(t)$ of Eq. (2.6), which is the Fourier transform of $g(\omega)$ evaluated from E_k. In order to evaluate the line shape, we must specify $g(\omega)$, which in general is a rather complicated function of ω. We expect, however, that the gross features of the line shape will not depend on the fine structure of $g(\omega)$. We therefore use relatively simple expressions for $g(\omega)$ or $g_k(t)$ while keeping a form which will resemble that of a real crystal.

The exciton band is assumed to have a width $2B$, with a mean energy E_M. The $\mathbf{k}=0$ state usually lies at the bottom of the band ($E_0=E_M-B$), or at the top of the band ($E_0=E_M+B$); in rare cases, the $\mathbf{k}=0$ state may lie in the center of the band. We will consider only bands symmetric around E_M.

The simplest $g(\omega)$ which we will treat is the Lorentzian

$$g(\omega)=\frac{B/\pi}{(\omega-E_M)^2+B^2}\ , \tag{3.1}$$

with

$$g_k(t)=e^{+i(E_k-E_M)t}\,e^{-B|t|}\ . \tag{3.2}$$

This density of states allows us to evaluate most of the necessary formulas directly and is therefore extremely useful. However, because it does not vanish outside a finite width and has a very long tail, its use can lead to incorrect results if proper care is not taken.

The density of states close to that of a three-dimensional exciton band and yet still manageable analytically is the hemicircular shape[5]

$$g(\omega)=\frac{2}{\pi B^2}\sqrt{B^2-(\omega-E_M)^2}\ ,\quad \text{for } E_M-B\le\omega\le E_M+B\ ,$$
$$=0\ ,\qquad \text{for}\begin{cases}\omega>E_M+B\\ \omega<E_M-B\end{cases}, \tag{3.3}$$

with

$$g_k(t)=\frac{2e^{+i(E_k-E_M)t}}{Bt}J_1(Bt)\ , \tag{3.4}$$

where $J_1(z)$ is the ordinary Bessel function of order one. This density of states mimics the square root dependence at the band edges and so is expected to give a good description of line shapes.

Other possible densities of states are Gaussian

$$g(\omega)=\frac{1}{B\sqrt{\pi}}e^{-(\omega-E_M)^2/B^2}\ , \tag{3.5}$$

with

$$g_k(t)=e^{+i(E_k-E_M)t}e^{-B^2t^2/4} \tag{3.6}$$

or the triangular or rectangular shapes. We will not discuss these less interesting forms, but note that they all lead to slight variations to the final results.

In the following discussion of line shapes, we will discuss only the Lorentzian and the hemicircular densities.

B. Line shapes

We are now in a position to evaluate line shapes by use of the above densities of states and Eq. (2.5). Let us define

$$I_k(t)\equiv\exp\left[-D^2\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\,e^{-\gamma\tau_2}g_k(\tau_2)\right]\ , \tag{3.7}$$

which can also be written

$$I_k(t)=\exp\left[-D^2\int_0^t d\tau_1(t-\tau_1)\,e^{-\gamma\tau_1}g_k(\tau_1)\right] \tag{3.8}$$

or

$$I_k(t)=\exp\left[-D^2e^{-\gamma t}\frac{\partial}{\partial\gamma}e^{\gamma t}\int_0^t g_k(\tau_1)\,e^{-\gamma\tau_1}d\tau_1\right]. \tag{3.9}$$

In the line shape formula, there are three energy parameters: B, the exciton bandwidth; D, the exciton phonon coupling strength; and γ, the inverse correlation time of the fluctuations (which should be related to the phonon dispersion). The line shape and position depend on the relative values of these parameters.[1]

1. $D\gg B$ or γ: Gaussian limit

In the limit that D is much larger than B or γ [the exact inequality will depend *slightly* on the assumed form for $g_k(t)$], the integral in the exponent of Eq. (3.7) or (3.8) for times $t\gtrsim 1/D$ will be $t^2/2$, i.e., for $t<1/D$, then $t\ll B^{-1}$ or γ^{-1}, so that $g_k(\tau_1)\,e^{-\gamma\tau_1}\simeq 1$. Thus,

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dt\,e^{i(\omega-E_k)t}e^{-D^2t^2/2}$$
$$=\frac{1}{D\sqrt{2\pi}}\exp-[(\omega-E_k)^2/2D^2]\ . \tag{3.10}$$

Thus, in this limit, the line shape is Gaussian with a width proportional to D [full width at half-maximum $=2(2\ln 2)^{1/2}D$], independent of the explicit form of $g(\omega)$.

2. $D\ll B$ or γ: Lorentzian limit

In the limit in which D is much smaller than B or γ, a different limiting form occurs. To study this case in its simplest guise, consider the *Lorentzian density of exciton states* [Eq. (3.1)]. Then,

$$I_k(t)=\exp\left[-D^2\int_0^t d\tau(t-\tau)\,e^{-\gamma\tau}e^{+iE_k\tau}e^{-B\tau}\right]\ , \tag{3.11}$$

where we have put $E_M=0$ for convenience. Then,

$$I_k(t)=\exp\left\{-\frac{D^2}{(\gamma+B-iE_k)^2}\left[-1+(\gamma+B-iE_k)\,t+e^{-(\gamma+B-iE_k)t}\right]\right\} \tag{3.12}$$

and

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dt\,e^{i(\omega-E_k)t}I_k(t)\ . \tag{3.13}$$

At short times $[t<(B+\gamma)^{-1}]$, the exponent in Eq. (3.12) is $D^2t^2/2<D^2(B+\gamma)^{-2}\ll 1$; at longer times $[t\gtrsim(\gamma+B)^{-1}]$, the exponent can be approximated as

$$-\frac{D^2}{(\gamma+B-iE_k)^2}\left[(\gamma+B-iE_k)t\right]\ . \tag{3.14}$$

Thus, in the limit that $(B+\gamma)\gg D$, the line shape is given by

$$I(\omega)=\frac{\Gamma_1/\pi}{(\omega-E_k-\Gamma_2)^2+\Gamma_1^2}\ , \tag{3.15}$$

i.e., a Lorentzian with width Γ_1 given by

$$\Gamma_1=\frac{D^2(B+\gamma)}{(B+\gamma)^2+E_k^2}\ , \tag{3.16}$$

and shift Γ_2 given by

$$\Gamma_2=\frac{+D^2E_k}{(B+\gamma)^2+E_k^2}\ . \tag{3.17}$$

If we had considered the hemicircular density of states [Eq. (3.3)], then we find, instead of Eq. (3.11),

$$I_k(t)=\exp\left[-D^2\int_0^t d\tau(t-\tau)\,e^{-\gamma\tau}\frac{2e^{+iE_k\tau}}{B\tau}J_1(B\tau)\right]\ . \tag{3.18}$$

Repeating the arguments below Eq. (3.13), we find that, in the limit $D\ll(B^2+\gamma^2)^{1/2}$ *and* $\gamma>0$, the line is again approximately Lorentzian of width

$$\Gamma_1=\frac{2D^2}{B^2}\left(\{[\gamma^2E_k^2+\tfrac14(\gamma^2+B^2-E_k^2)^2]^{1/2}\right.$$
$$\left.+\tfrac12(\gamma^2+B^2-E_k^2)\}^{1/2}-\gamma\right) \tag{3.19}$$

and shift

$$\Gamma_2 = +\frac{2D^2}{B^2}\left(\{[\gamma^2 E_k^2 + \tfrac{1}{4}(\gamma^2 + B^2 - E_k^2)^2]^{1/2} - \tfrac{1}{2}(\gamma^2 + B^2 - E_k^2)\}^{1/2}(-\operatorname{sign}E_k) + E_k\right). \tag{3.20}$$

This is rather complicated, but in the simple case $E_k = 0$ i.e., at the center of the band), then

$$\Gamma_1(E_k = 0) = \frac{2D^2}{B^2}\left[(B^2 + \gamma^2)^{1/2} - \gamma\right], \tag{3.21}$$

$$\Gamma_2(E_k = 0) = 0, \tag{3.22}$$

so that, for $B \gg \gamma$, $\Gamma_1 \simeq 2D^2/B$ and for $B \ll \gamma$, $\Gamma_1 \simeq D^2/\gamma$. These are the familiar motional narrowing results of Kubo,[9] Anderson,[12] and Sumi,[1] and agree with the results of Eqs. (3.16) and (3.17). If we interpret γ as a measure of the phonon bandwidth (or dispersion), then the simple golden rule formula for Γ_1 gives $D^2/\Delta E$, where D^2 is the square of the perturbation matrix element and $(\Delta E)^{-1}$ is the relevant density of states $\Delta E \alpha B$ if the exciton bandwidth is larger than the phonon bandwidth, and $\Delta E \alpha \gamma$ in the opposite case.

For $E_k \approx \pm B$ (top or bottom of the band), we have to be careful of Eqs. (3.19) and (3.20), because the approximation leading from Eq. (3.18) may break down when γ/B is small; moreover, the exciton density of states is so small near $E_k = \pm B$ that we must not trust the results obtained using the Lorentzian density of states (which has the incorrect form at the band edge). On the other hand, for $(\gamma/B) \gg 1$, we can trust Eqs. (3.19), (3.20), (3.16), and (3.17) near $E_k = \pm B$, where they lead to Lorentzian lines with

$$\Gamma_1(E_k = \pm B) \simeq D^2/\gamma \qquad (\gamma/B \gg 1), \tag{3.23}$$

$$\Gamma_2(E_k = \pm B) = D^2 E_k/\gamma^2 \quad (\gamma/B \gg 1). \tag{3.24}$$

In the limit that $(\gamma/B) < 1$, but $\gamma > 0$, we use Eqs. (3.19) and (3.20) (i.e., the hemicircular density of exciton states) in the form

$$\Gamma_1(E_k = \pm B) \cong \frac{2D^2\gamma}{B^2}\left(\{[(B/\gamma)^2 + \tfrac{1}{4}]^{1/2} + \tfrac{1}{2}\}^{1/2} - 1\right), \tag{3.25}$$

$$\Gamma_2(E_k = \pm B) \cong \mp\frac{2D^2}{B}\{[(\gamma^2/B^2 + \gamma^4/4B^4)^{1/2} - \gamma^2/2B^2]^{1/2} - 1\}. \tag{3.26}$$

These results will be examined and compared to Sumi's below.

3. *Static fluctuations:* $\gamma = 0$, $E_k = \pm B$

In the case that $\gamma = 0$, the static fluctuation case, for $E_k = -B$ (the bottom of the band), we find, in the case of a hemicircular density of states,

$$I_k(t) = \exp\left[-D^2\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \frac{2J_1(B\tau_2)}{B\tau_2} e^{-iB\tau_2}\right]. \tag{3.27}$$

The integrations can be performed exactly in this case (see Appendix C) and we find

$$I_k(t) = \exp\frac{2D^2}{B^2}\{iBt - i2Bt\, e^{-iBt}[J_0(Bt) + iJ_1(Bt)] + 1 - e^{-iBt}J_0(Bt)\}. \tag{3.28}$$

If $D \ll B$, then only the long time limit of $I_k(t)$ is important in determining the integral $(tB \gg 1)$ so that

$$I_k(t) \sim \exp\frac{2D^2}{B^2}\left[-\frac{2t^{1/2}B^{1/2}}{\pi^{1/2}}(1+i) + itB\right]. \tag{3.29}$$

The line shape is then *non*-Lorentzian

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\int_0^\infty dt\, e^{i[\omega + B + (2D^2/B)]t} \times \exp\left[-\frac{4D^2 t^{1/2}(1+i)}{B^{3/2}\pi^{1/2}}\right]. \tag{3.30}$$

In Appendix C. this integral is written in terms of exponentials and we find the full width at half-maximum to be proportional to D^4/B^3, in agreement with Sumi. At this level of approximation, the line falls off more quickly on the low energy side of the peak than on the high energy side.

C. Comparison to earlier results

In order to compare our results to those of Sumi (for the same model Hamiltonian), we define the line narrowing factor

$$\eta = \frac{\text{FWHM}}{2\sqrt{2\ln 2 D^2}} = \frac{\text{FWHM}}{(2.36D)}. \tag{3.31}$$

This is the ratio of the full width at half-maximum of the absorption line for a particular set of B, D, and γ values to that for the Gaussian line $(D^2 \gg B^2 + \gamma^2)$. Sumi[1] plots η for various values of B/γ as a function of $D/(B^2 + \gamma^2)^{1/2}$. To facilitate a comparison, we give formulas for η at the band edge in the case $D^2 \ll B^2 + \gamma^2$ for various values of B/γ using the hemicircular density of states [cf. Eq. (3.19)]

$$\begin{aligned} B/\gamma &= 0, & \eta &= 0.85D/(B^2+\gamma^2)^{1/2},\\ B/\gamma &= 1, & \eta &= 0.65D/(B^2+\gamma^2)^{1/2},\\ B/\gamma &= 10, & \eta &= 0.38D/(B^2+\gamma^2)^{1/2},\\ B/\gamma &= 100, & \eta &= 0.15D/(B^2+\gamma^2)^{1/2}. \end{aligned} \tag{3.32}$$

As shown in Table I, these results agree quantitatively with Sumi.[1]

In the static case, in which $\gamma = 0$, we find a very asymmetric line (see Appendix C) whose *upper* half-width is $3.67D^4/B^3$ (Sumi reports $3.18D^4/B^3$) and whose

TABLE I. Line narrowing factor for a hemicircular density of exciton states as a function of D/γ and B/γ $[D^2 \ll (B^2+\gamma^2)]$.

D/γ	B/γ	$\log\eta(E_k=0)$	$\log\eta(E_k=\pm B)$	$\log\eta(E_k=-B)$[a]
0.1	0	−1.07	−1.07	−1.08
	1	−1.15	−1.34	−1.35
	10	−1.81	−2.42	−2.40
	100	−2.70	−3.81	−3.77
0.01	0	−2.07	−2.07	−2.08[b]
	1	−2.15	−2.34	−2.35
	10	−2.81	−3.42	−3.40
	100	−3.70	−4.81	−4.77

[a]From Sumi.[(1)]
[b]Extrapolated from Fig. 2 of Sumi.[(1)]

lower half-width is $0.97D^4/B^3$ (Sumi reports $0.61D^4/B^3$). In addition, we find the peak position shifted by $2D^2/B$ to the red, again in agreement with Sumi. As remarked above, the line is very asymmetric, falling very slowly on the blue end of the peak.

IV. EXCITON DYNAMICS

The nature of exciton motion will be characterized by whether the mean free path of the exciton in a **k** state $l(\mathbf{k})$ is greater or less than a lattice constant $|\mathbf{a}|$. If $l(\mathbf{k}) > |\mathbf{a}|$, we will call it *band* motion and if $l(\mathbf{k}) < |\mathbf{a}|$, we will call it hopping motion.

As we saw in Sec. II, the factor relating $d\tilde{\sigma}_{kk}/dt$ to $\tilde{\sigma}_{kk}$ is related to the real part of the factor in the exponent of $I_k(t)$ [compare Eqs. (2.5) and (2.10)]. For long times, this factor is the inverse of the scattering time out of the state with wave vector **k** (i.e., for long times, $d\tilde{\sigma}_{kk}/dt = -\tilde{\sigma}_{kk}\tau_k^{-1}$). Thus,

$$\Gamma_{kk} \equiv \tau_k^{-1} = 2D^2 \operatorname{Re} \int_0^\infty d\tau\, e^{-\gamma\tau} g_k(\tau) \tag{4.1}$$

and

$$\hat{l}(k) \equiv l(\mathbf{k})/|\mathbf{a}| = \frac{v(\mathbf{k})}{\Gamma_{kk}|\mathbf{a}|} \cong \frac{B}{\Gamma_{kk}} , \tag{4.2}$$

where we have set the velocity of the exciton $v(\mathbf{k})$ approximately equal to half the bandwidth multiplied by the lattice constant. This is valid near the band center $E_k \approx 0$.

For $E_k = 0$ and a Lorentzian density of exciton states,

$$\Gamma_{kk} = 2D^2/(B+\gamma) , \tag{4.3a}$$

$$\hat{l}(k) = \tfrac{1}{2}B(B+\gamma)/D^2 , \tag{4.3b}$$

so that, for $B/\gamma \ll 1$, $\hat{l}(k) \gg 1$ if $B \gg D^2/\gamma$ and $\hat{l}(k) \ll 1$ if $B \ll D^2/\gamma$. This represents the Haken–Strobl[3] limit, because, for $B/\gamma \ll 1$,

$$\langle V_{nn}(t)\, V_{nn}\rangle \to (D^2/\gamma)\, \delta(t) , \tag{4.4}$$

in agreement with their assumptions. Physically, this corresponds to the limit in which the phonon bandwidth ($\sim\gamma$) is much larger than the exciton bandwidth ($\sim B$). In this limit, the transport is bandlike if $B \gg D^2/\gamma$ and hoppinglike if $B \ll D^2/\gamma$.

In the case of general B/γ, we find $\hat{l}(k) \gg 1$ whenever

$$(B/D) > -\tfrac{1}{2}(\gamma/D) + \sqrt{2 + \tfrac{1}{4}(\gamma/D)^2} \tag{4.5}$$

(for $E_k = 0$ and a Lorentzian density of states). Thus, for $\gamma/D = 0$, $(B/D) > \sqrt{2}$ and for $\gamma/D = 1$, $B/D > 1$. From Sumi's analysis,[1] he finds, for $\gamma/D = 0$, $(B/D) \gtrsim 0.95$ and for $\gamma/D = 1$, $B/D \gtrsim 0.7$. Thus, the Lorentzian density of states gives good agreement with these results. The slight difference between Sumi's results and ours is that his criterion for the change from band to hopping is $\Gamma_{kk} = 2B$. Thus, his results for the limiting values of (B/D) are approximately a factor of $2^{-1/2}$ those of ours. For $E_k = 0$ and a hemicircular density of states, we find

$$\Gamma_{kk} = \frac{4D^2}{B^2}\left[(B^2+\gamma^2)^{1/2} - \gamma\right] , \tag{4.6a}$$

$$\hat{l}(k) = \frac{B^3}{4D^2} \frac{1}{\left[(B^2+\gamma^2)^{1/2} - \gamma\right]} , \tag{4.6b}$$

so that, for $\gamma/D = 0$, $\hat{l}(k) > 1$ for $B/D > 2$ and for $\gamma/D = 1$, $\hat{l}(k) > 1$ for $B/D \gtrsim 1.1$. Thus, these results are again in good agreement with those of Sumi.

The mean free path depends on E_k in a rather complicated manner; however, for E_k near the band edges, the critical value of B/D decreases slightly. This decrease is small enough so that for qualitative results it is unimportant.

V. SUMMARY AND CONCLUSIONS

The analysis presented in this paper is a straightforward application of the usual theories of line shapes and exciton dynamics. We have, following Sumi[1] and Toyozawa,[4] introduced three energy parameters in the Hamiltonian: (1) the decay rate of the exciton phonon fluctuations γ which can be taken to be a measure of the phonon bandwidth; (2) the exciton bandwidth $2B$; and (3) the amplitude of the exciton phonon fluctuations D. Assuming that the exciton phonon coupling is a Gaussian–Markov process (with correlation time γ^{-1}) leads to an integral expression for the line shape and to a stochastic Liouville equation for the exciton density matrix.

In the limit $D^2 \gg B^2 + \gamma^2$, a Gaussian optical line results with half-width $\sqrt{2\ln 2}\,D$. In the opposite limit, the optical line width becomes narrower (motional narrowing) and the peak shifts. As $\gamma/D \to \infty$, the exciton phonon correlation function becomes a delta function of height D^2/γ and the optical line becomes a Lorentzian of the half-width D^2/γ. In the limit that B/D gets very large (but $\gamma \neq 0$), the line becomes Lorentzian (of half-width $2D^2/B$ for the band center).

As pointed out by Toyozawa and Sumi,[1] the $\gamma/D \to \infty$ limit is that treated by Haken and Strobl[3] and Haken and co-workers.[3] In the limit $B \to 0$, the present theory reduces to that of Kubo.[6]

The analysis presented here does not rely on the dynamical coherent potential approximation of Sumi,[1] but instead on various approximations to the integrals appearing in the line shape function. This shows the general behavior which comes out of this model without much computation.

The present analysis can be extended and improved in a number of ways. First, the nondiagonal fluctuations can be treated [i.e., $\langle V_{nm}(t)V_{nm}\rangle$] in the same manner. Although this is straightforward, it is tedious and introduces some complications. It is best left to another note. Secondly, the Urbach rule, which comes out of Sumi's analysis, can be retrieved by our analysis only with more computation, which we felt would obscure the general point of this paper.

APPENDIX A: OPTICAL LINE SHAPE FORMULAS

We begin with Eq. (2.4):

$$\frac{d}{dt}\, a_k(t) = i\left[H_0^X + V^X(t)\right] a_k(t) . \tag{A1}$$

In the interaction representation defined as

$$\tilde{a}_k(t) = e^{-iH_0^X t} a_k(t) = e^{-iH_0 t} a_k(t) e^{+iH_0 t} , \quad \text{(A2)}$$

we find

$$\frac{d}{dt}\tilde{a}_k(t) = i\tilde{V}^X(t)\,\tilde{a}_k(t) , \quad \text{(A3)}$$

where

$$\tilde{V}(t) \equiv e^{-iH_0 t} V(t)\, e^{iH_0 t} . \quad \text{(A4)}$$

Thus,

$$\tilde{a}_k(t) = \exp_T\left[i\int_0^t \tilde{V}^X(\tau)\,d\tau\right] a_k(0) , \quad \text{(A5)}$$

where the subscript refers to the usual time ordered exponential. We may then write

$$\langle \tilde{a}_k(t)\rangle = \left\langle \exp_T\left[i\int_0^t \tilde{V}^X(\tau)\,d\tau\right]\right\rangle a_k(0) . \quad \text{(A6)}$$

The usual definition of the moments $M_n(t)$ and the cumulants $K_n(t)$ is[6,8]

$$\left\langle \exp_T\left[i\int_0^t \tilde{V}^X(\tau)\,d\tau\right]\right\rangle \equiv \sum_{n=0}^{\infty} \tilde{M}_n(t) \equiv \exp_T\left[\sum_{n=1}^{\infty} \tilde{K}_n(t)\right] . \quad \text{(A7)}$$

For a Gaussian process, only the first two cumulants are nonzero:

$$\tilde{K}_1(t) = \tilde{M}_1(t) = i\int_0^t d\tau\,\langle V^X(\tau)\rangle , \quad \text{(A8)}$$

$$\tilde{K}_2(t) = \tilde{M}_2(t) - \tfrac{1}{2}T\,[\tilde{M}_1(t)]^2$$
$$= -\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left[\langle \tilde{V}^X(\tau_1)\tilde{V}^X(\tau_2)\rangle - \langle \tilde{V}^X(\tau_1)\rangle\langle \tilde{V}^X(\tau_2)\rangle\right] . \quad \text{(A9)}$$

We now use the explicit potential form of Eqs. (1.2) and (1.4). In the momentum representation,

$$V(t) = \sum_n V_{nn}(t)\, a_n^+ a_n = \sum_{kk_1} V_{kk_1}(t)\, a_k^+ a_{k_1} . \quad \text{(A10)}$$

Thus

$$\tilde{V}(t) = \sum_{kk_1} V_{kk_1}(t)\, e^{-i(E_k - E_{k_1})t}\, a_k^+ a_{k_1} \quad \text{(A11)}$$

and, from Eq. (1.2), $\langle V_{kk_1}(t)\rangle = 0$; thus $\tilde{M}_1(t) = \tilde{K}_1(t) = 0$. Evaluating $\tilde{K}_2(t)$, we need

$$\langle V_{k_1k_2}(t) V_{k_3k_4}(t_1)\rangle = \frac{D^2}{N} e^{-\gamma|t-t_1|}\,\delta_{k_1+k_3,k_2+k_4} \quad \text{(A12)}$$

and therefore

$$\langle \tilde{V}^X(t)\tilde{V}^X(t_1)\rangle = \frac{D^2}{N} e^{-\gamma|t-t_1|} \sum_{k_1k_2k_3k_4} \delta_{k_1+k_3,k_2+k_4}\, e^{i(E_{k_2}-E_{k_1})t}\, e^{i(E_{k_4}-E_{k_3})t_1} (a_{k_1}^+ a_{k_2})^X (a_{k_3}^+ a_{k_4})^X . \quad \text{(A13)}$$

Now, consider the time dependence of $\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle$ in order to find $I_k(\omega)$:

$$\frac{d}{dt}\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle \equiv \frac{d}{dt}\left[e^{+iE_k t}\langle 0|\langle a_k(t)\rangle a_k^+|0\rangle\right]$$
$$= \langle 0|[\dot{\tilde{K}}_2(t)\langle \tilde{a}_k(t)\rangle] a_k^+|0\rangle , \quad \text{(A14)}$$

with

$$\dot{\tilde{K}}_2(t) = -\int_0^t d\tau\,\langle \tilde{V}^X(t)\tilde{V}^X(\tau)\rangle . \quad \text{(A15)}$$

Since $\langle 0|a_{k'}^+$ vanishes for any k', we find

$$\frac{d}{dt}\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle = \frac{-D^2}{N}\int_0^t d\tau\, e^{-\gamma|t-\tau|} \times \sum_{k_1} e^{i(E_k - E_{k_1})(t-\tau)}\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle . \quad \text{(A16)}$$

Integrating Eqs. (A16), we find

$$\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle = \exp\left[-D^2\int_0^t d\tau \int_0^{\tau} d\tau_1\, e^{-\gamma\tau_1} g_k(\tau_1)\right] , \quad \text{(A17)}$$

where $g_k(\tau)$ is given by Eq. (2.6). Thus,

$$\langle 0|\langle \tilde{a}_k(t)\rangle a_k^+|0\rangle = e^{-iE_k t}\exp\left[-D^2\int_0^t d\tau \int_0^{\tau_1} d\tau_1\, e^{-\gamma\tau_1} g_k(\tau_1)\right] \quad \text{(A18)}$$

and $I_k(\omega)$ is given by

$$I_k(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^{\infty} dt\, e^{i(\omega - E_k)t} \times \exp\left[-D^2\int_0^t d\tau\int_0^{\tau_1} d\tau_1\, e^{-\gamma\tau_1} g_k(\tau_1)\right] . \quad \text{(A19)}$$

APPENDIX B: EXCITON DENSITY MATRIX EQUATIONS OF MOTION

Starting from the equation of motion of the density matrix

$$\dot{\rho}(t) = -i[H_0^X + V^X(t)]\,\rho(t) \quad \text{(B1)}$$

and the definition of the interaction representation

$$\tilde{\tilde{\rho}}(t) = e^{iH_0^X t}\rho(t) = e^{iH_0 t}\rho(t)\, e^{-iH_0 t} , \quad \text{(B2)}$$

we find

$$\frac{d}{dt}\tilde{\tilde{\rho}}(t) = -i\tilde{\tilde{V}}^X(t)\,\tilde{\tilde{\rho}}(t) , \quad \text{(B3)}$$

where

$$\tilde{\tilde{V}}(t) = e^{iH_0^X t}\, V(t) . \quad \text{(B4)}$$

Thus

$$\tilde{\tilde{\sigma}}(t) = \langle \tilde{\tilde{\rho}}(t)\rangle = \left\langle \exp_T\left[-i\int_0^t \tilde{\tilde{V}}^X(\tau)\right]\right\rangle \sigma(0) . \quad \text{(B5)}$$

Using the Gaussian nature of $V(t)$ and Eq. (1.2), we find that only the second cumulant is nonzero, so that

$$\tilde{\tilde{\sigma}}(t) = \exp_T[+\tilde{\tilde{K}}_2(t)]\,\sigma(0) , \quad \text{(B6)}$$

with

$$\tilde{\tilde{K}}_2(t) = -\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \tilde{\tilde{V}}^x(\tau_1)\tilde{\tilde{V}}^x(\tau_2)\rangle \ . \quad \text{(B7)}$$

Thus, we find, using the generalized cumulant of Freed[7] and Kubo,[6]

$$\frac{d\tilde{\tilde{\sigma}}}{dt} = \dot{\tilde{\tilde{K}}}_2(t)\,\tilde{\tilde{\sigma}}(t) \ . \quad \text{(B8)}$$

The diagonal elements in the k representation, which diagonalizes H_0, are then given by [using Eq. (A13)]

$$\frac{d}{dt}\tilde{\tilde{\sigma}}_{kk}(t) = -\int_0^t d\tau \langle 0|a_k[\langle \tilde{\tilde{V}}^x(t)\tilde{\tilde{V}}^x(\tau)\rangle\,\tilde{\tilde{\sigma}}(t)]\,a_k^+|0\rangle$$

$$= -\int_0^t d\tau \frac{D^2}{N} e^{-\gamma|t-\tau|} \sum_{k_1k_2k_3k_4} \delta_{k_1+k_3,k_2+k_4} \exp[i(E_{k_1}-E_{k_2})t + i(E_{k_3}-E_{k_4})\tau]\langle 0|a_k[a_{k_1}^+a_{k_2},[a_{k_3}^+a_{k_4},\tilde{\tilde{\sigma}}(t)]]\,a_k^+|0\rangle \ , \quad \text{(B9)}$$

where we have assumed that $\langle V(\tau_1)V(\tau_2)\rangle = \langle V(\tau_2)V(\tau_1)\rangle$. Evaluating the matrix elements in Eq. (B9), we find

$$\frac{d}{dt}\tilde{\tilde{\sigma}}_{kk}(t) = -\tilde{\tilde{\sigma}}_{kk}(t)\left[\int_0^t d\tau\, 2D^2 e^{-\gamma\tau}\frac{1}{N}\,\mathrm{Re}\sum_{k_1} e^{i(E_k-E_{k_1})\tau}\right] + \sum_{k_1}\tilde{\tilde{\sigma}}_{k_1k_1}(t)\int_0^t d\tau\, 2D^2 e^{-\gamma\tau}\frac{1}{N}\,\mathrm{Re}(e^{i(E_k-E_{k_1})\tau}) \ , \quad \text{(B10)}$$

which is equivalent to Eq. (2.10). We note that the factor in front of $\tilde{\tilde{\sigma}}_{kk}(t)$ on the right-hand side of Eq. (B10) is twice the real part of the factor in front of $\langle 0|\langle\tilde{a}_k(t)\rangle\, a_k^+|0\rangle$ on the right-hand side of Eq. (A16).

APPENDIX C: LINE SHAPE CALCULATIONS

In Sec. III, in the discussion of the limiting case $D \ll B$ or γ, we found Lorentzian line shapes. Using a density of exciton states which is of Lorentzian form, we found [see Eq. (3.12)] that

$$I_k(t) = \exp\left\{\frac{-D^2}{(B+\gamma-iE_k)^2}\left[-1+(\gamma+B-iE_k)t + e^{-(\gamma+B-iE_k)t}\right]\right\} \quad \text{(C1)}$$

and

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty dt\, e^{i(\omega-E_k)t} I_k(t) \ . \quad \text{(C2)}$$

For times short compared to $(B+\gamma)^{-1}$, the exponent in Eq. (C1) is of order $D^2t^2 \ll 1$ [in the case $D \ll (B+\gamma)$] so that $I_k(t) \approx 1$ for $t < (B+\gamma)^{-1}$. For $t > (B+\gamma)^{-1}$, the exponent is

$$-D^2(B+\gamma+iE_k)t/[(B+\gamma)^2+E_k^2] \ .$$

For $|\omega - E_k| < (B+\gamma)$, we can use the long time form of $I_k(t)$ in Eq. (C2), so that

$$I(\omega) \cong \frac{D^2(B+\gamma)/\pi[(B+\gamma)^2+E_k^2]}{\{\omega - E_k - D^2E_k/[(B+\gamma)^2+E_k^2]\}^2 + \{D^2(B+\gamma)/[(B+\gamma)^2+E_k^2]\}^2} \ , \quad \text{(C3)}$$

which is Eq. (3.15) *et seq.*

In the case that we use a hemicircular form for the density of exciton states, we find [Eq. (3.18)]

$$I_k(t) = \exp\left[-D^2\int_0^t d\tau(t-\tau)\, e^{-\gamma\tau}e^{iE_k\tau}\, 2J_1(B\tau)/B\tau\right] . \quad \text{(C4)}$$

In the case that $D^2 \ll B^2 + \gamma^2$, we again may use the long time limit in $I_k(t)$ for $I(\omega)$ when $|\omega - E_k| \lesssim (B^2+\gamma^2)^{1/2}$, so that

$$I_k(t) \cong \exp - \left[D^2 t\int_0^\infty d\tau\, e^{-\gamma\tau} e^{iE_k\tau}\frac{2J_1(B\tau)}{B\tau}\right] \quad \text{(C5)}$$

as long as $\gamma > 0$. If γ/B is small, then

$$\int_0^\infty d\tau\,\tau\, e^{-\gamma\tau}e^{iE_k\tau}\frac{2J_1(B\tau)}{B\tau} = \frac{2}{B^2}\,\frac{[\sqrt{(\gamma-iE_k)^2+B^2}-(\gamma-iE_k)]}{\sqrt{(\gamma-iE_k)^2+B^2}}$$

can become very large as $E_k \to \pm B$; in fact, for $E_k = \pm B$, it diverges as $\gamma \to 0$. Therefore, great care must be taken for $\gamma \to 0$ and $E_k = \pm B$. In any other case, the approximations leading to Eq. (C5) are valid and $I(\omega)$ is the Lorentzian with half-width given by Eq. (3.19) and shift given by Eq. (3.20).

In the case $\gamma = 0$, $E_k = \pm B$ (the static, band edge limit), we find

$$I_k(t) = \exp\left[-D^2\int_0^t d\tau_1\int_0^{\tau_1} d\tau_2\, e^{-iB\tau_2}\frac{2J_1(B\tau_2)}{B\tau_2}\right] \quad \text{(C6)}$$

$$= \exp - D^2\int_0^t d\tau_1\frac{2}{B}\{-i - e^{-iB\tau_1}[J_1(B\tau_1) - iJ_0(B\tau_1)]\} \ ,$$

where we have used formula (11.3.10) of Abramowitz and Stegun.[13] Thus,

$$I_k(t) = \exp\left\{\frac{-2D^2}{B^2}\left[-iBt - \int_0^{Bt} dz\, e^{-iz}[J_1(z) - iJ_0(z)]\right]\right\} . \quad \text{(C7)}$$

Using formulas (11.3.9) and (11.3.4) of Abramowitz and Stegun,[13] we find

$$I_k(t) = \exp\left(\frac{2D^2}{B^2}\{iBt - 2iBt\, e^{-iBt}[J_0(Bt) + iJ_1(B\tau)] + 1 - e^{-iBt}J_0(Bt)\}\right) , \quad \text{(C8)}$$

which is identical to Eq. (3.28). For $|\omega - E_k| < B$ and

$D^2 \ll B^2$, we need only the long time form of Eq. (C8) for $I(\omega)$. Using the asymptotic behavior of $J_n(z)$.[13]

$$I_h(t) \cong \exp \frac{2D^2}{B^2}\left[-2\left(\frac{Bt}{\pi}\right)^{1/2}(1+i)+iBt\right] \tag{C9}$$

and

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dt\, e^{i(\omega+B+2D^2/B)t}\exp\left[-\frac{4D^2}{B^2}\left(\frac{Bt}{\pi}\right)^{1/2}(1+i)\right]. \tag{C10}$$

Defining $X=\omega+B+2D^2/B$ and $K=4D^2/(B^3\pi)^{1/2}$, we substitute

$$z=(1+i)t^{1/2}, \quad \text{for } X<0 ,$$

so that

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\lim_{R\to\infty}\int_{(1+i)0}^{(1+i)R} dz\,\frac{z}{i}\, e^{Xz^2/2}e^{-Kz}. \tag{C11}$$

Closing the contour by going from $(1+i)R$ to R and from R to 0, we find [since for R large the contribution vanishes from the line integral from $(1+i)R$ to R]

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dz\frac{z}{i}\, e^{Xz^2/2}e^{-Kz}=0, \quad \text{for } X<0 . \tag{C12}$$

For $X>0$, substitute $z=(1-i)t^{1/2}$ and

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\lim_{R\to\infty}\int_{(1-i)0}^{(1-i)R} iz\,dz\, e^{-Xz^2/2}e^{-iKz}. \tag{C13}$$

Closing the contour by going from $(1-i)R$ to R and from R to 0, we find [again noting that the contribution vanishes along the line $(1-i)R$ to R]

$$I(\omega)=\frac{1}{\pi}\int_0^\infty dz\, z\sin Kz\, e^{-Xz^2/2}=\frac{K}{(2\pi X^3)^{1/2}}e^{-K^2/2X}. \tag{C14}$$

Thus, the optical line is very unsymmetric, vanishing below $\omega=-B-2D^2/B$, with a peak at $\omega\cong-B-(2D^2/B)+16[D^4/(3\pi B^3)]$ and falling off very slowly to the blue. Using Eq. (C14), we can find the *upper* half-width (i.e., the frequency above the peak at which the intensity is half the peak height) and the lower half-width. Writing these frequencies as $\omega_h=K^2\alpha$, we find

$$\alpha^{3/2}e^{1/2\alpha}=2e^{3/2}/3^{3/2} ,$$

so that $\alpha\approx 0.15$ and $\alpha\approx 1.05$. Since the peak is at $\alpha=0.33$, we find that the upper half-width W_1 is $0.72K^2 \cong 3.67D^4/B^3$ and the lower half-width W_2 is $0.19K^2 = 0.97D^4/B^3$.

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