Research Article

Correlating exciton coherence length, localization, and its optical lineshape

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The lineshapes of spectroscopic transitions offer windows into the local environment of a system. Here, we present a novel approach for connecting the lineshape of a molecular exciton to finite-temperature lattice vibrations. Our results are based upon an exact, self-consistent treatment of a continuous model in which thermal effects are introduced as fluctuations about the zero-temperature localized soliton state. Two parameters enter our model: the exciton band-width (J) and the exciton reorganization energy μ. Our model bridges the strongly localized limit where the exciton homogeneous line width is observed to be independent of temperature and the molecular aggregate limit in which the line width increases linearly in temperature.

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I. Introduction

One of the the fundamental issues in the materials science of disordered semiconductors is in the unravelling optical and electronic properties from disordered energy landscapes and correlating these to complex solid-state microstructures. In polymeric semiconductors in particular, the structure-property interdependence is such that the excitation spectral line shapes are governed by the interplay between inter- and intra-chain electronic interactions both of which are highly sensitive to the local microstructures of the system. Within the Kubo-Anderson model, the homogeneous lifetime is related to the variance or fluctuations in the spectroscopic energy level and the correlation time of the fluctuations via.

$$T_2 = (\Delta^2 \tau_c)^{-1}.^{[1][2][3]}$$

It is desirable to relate both Δ^2 and τ_c to the properties of the material substrate.

It was suggested in Ref.[4] following arguments in Ref.[5] that the lineshape in polycrystaline polymeric semiconductors could be interpreted in the context of a weakly coupled aggregate model; a simple two-dimensional free-exciton model of an aggregate composed of polymer chains with a persistence length ℓ_x that are assembled to form a lamellar stack of persistence length ℓ_y. Excitonic coupling effects, both along and between the chains, can be described by an intrachain (parallel) hopping integral $J_\parallel$, and an interchain (perpendicular) hopping integral $J_\perp$. Using a two-dimensional free exciton model we showed the ratio of the homogeneous linewidths (γ) of the isolated (single chain) to the aggregate is related to delocalization along each direction.

$$r = \frac{\gamma_{iso}}{\gamma_{agg}} = \frac{J_\parallel}{J_\perp} \left(\frac{\ell_\perp}{\ell_\parallel} \right)^2 \tag{1}$$

Consequently, by taking the ratio of the homogeneous line-widths for the isolated vs. aggregate system, one obtains a succinct measure of the localization of the exciton. However, the model is based upon a simple free-exciton model, essentially a particle-in-a-box, where one expands the approximately parabolic energy bands about the super-radiant transition giving $\gamma_{homo} \propto |J|/(\ell)^2$. This is expected to be true in the high-temperature limit where the exciton momentum is no longer a good quantum number and localization is due to dynamical disorder. At low temperature, however, the lineshape reflects the static localization due to the static disorder. This trend is observed in studies of cyanine dye J-aggregate films (Ref. [5]) in which it is reported that the dynamical scattering limit persists even down to 9K with no transition to the static disorder limit.

In this paper, we revisit this model with the goal of correlating the exciton lineshape with its localization length taking into account static and dynamic disorder at finite temperature. For this, we present exciton models in which energy fluctuations are introduced in terms of local site energy fluctuations and include the effect of self-trapping whereby the initial exciton localization is due to coupling to the lattice phonons. We then introduce finite-temperature fluctuations around the $T = 0K$ self-trapped excition (STE) state and consider how the STE picture is modified at finite temperature. Our results are based upon a numerically exact, self-consistent treatment of the Davydov soliton model[6] in which thermal effects are introduced as excitations about the zero-temperature soliton state. We find that both the energy fluctuations and the exciton localization can be described in terms of a parameter-free, reduced description, by introducing a critical temperature below which exciton self-trapping is expected to be stable. Above this temperature, the self-consistent ansatz relating the lattice distortion to the exciton wave function breaks down.

II. Theoretical models

A. Free exciton limit

The central issue of this paper concerns the connection between dynamic disorder and the homogeneous line width of molecular excitons. To set the framework for our discussion, we begin with a basic finite 1D lattice exciton model described by

$$H = \sum_{n=0}^{N-1} E_n |n\rangle\langle n| + J \sum_{n=0}^{N-1} (|n+1\rangle\langle n| + |n\rangle\langle n+1|), \tag{2}$$

in which $|n\rangle$ represents a local excitation on site n with energy E_n and J is the hopping integral between nearest neighbors. For this analysis, we take all the sites to be identical. For J-aggregates, $J < 0$ such that the lowest-energy exciton transition corresponds to a super-radiant state. We can easily diagonalize H:

$$E_k = E_o + 2J \cos\left(\frac{\pi k}{N+1}\right) \tag{3}$$

where $k = 1, \cdots N$ is a quantum number and with states

$$|k\rangle = \left(\frac{2}{N+1}\right)^{1/2} \sum_{n=1}^{N} \sin\left(\frac{kn\pi}{N+1}\right) |(n-1)\rangle. \tag{4}$$

In principle, the local site energies are not homogeneous due to local static and dynamic disorder effects. If we treat the local energy fluctuations as a time-dependent perturbation, then the exciton energy levels acquire a fluctuation given by first-order perturbation theory

$$\delta E_k = \langle k|H_{rnd}|k\rangle \tag{5}$$

$$= \frac{2}{N+1} \sum_{n=1}^{N} \sin^2\left(\frac{kn\pi}{N+1}\right) \delta\epsilon_n(t), \tag{6}$$

where H_{rnd} is the random noise term in our model. If we assume that all the noise terms are uncorrelated and follow from an Ornstein-Uhlenbeck (Brownian noise) process,

$$\langle \delta\epsilon_n(t)\delta\epsilon_{n'}(t')\rangle = \delta_{nn'}\sigma^2 e^{-|t-t'|/\tau_c}, \tag{7}$$

in which the fluctuation-dissipation theorem relates the variance in the noise to the relaxation time $\sigma^2 = kT/\tau_c$. Using this, write

$$\langle \delta E_k(t)\delta E_k(0)\rangle = \frac{kT}{\tau_c} e^{-|t|/\tau_c} \left(\frac{2}{N+1}\right)^2 \sum_{n=1}^{N} \sin^4\left(\frac{kn\pi}{N+1}\right)$$

$$= \frac{3}{2(N+1)} \frac{kT}{\tau_c} e^{-|t|/\tau_c}. \tag{8}$$

Note that the summation is simply the inverse-participation ratio (IPR) for the exciton state, $\ell^{-1} = 3/2(N+1)$. The reciprocal of IPR gives the number of sites participating in the final eigenstate. If the exciton is fully delocalized over all N sites, then $\ell \approx N$ sites and the site-wise contribution to the wavefunction is simply $1/\ell$.

In other words, as the exciton is delocalized over an increasingly larger domain size, the local energy landscape becomes smooth and gives a vanishing contribution to the homogeneous broadening. Hence, the line-shape is expected to become progressively narrower as the exciton is further delocalized. This is often referred to as *exchange narrowing*. Under this model, the exciton hopping integral J plays no role whatsoever in determining the lineshape.

We can also introduce the effect of thermal fluctuations by expanding E_k about the lowest-energy transition (corresponding to quantum number $k = 1$) and introducing fluctuations $k - 1 \to \delta k(t)$

$$E(t) = \left(E_o + 2J\cos(\ell^{-1})\right) - \delta k(t)\frac{2J}{\ell}\sin(\ell^{-1}) + \cdots \tag{10}$$

where we write $\ell^{-1} = \pi/(N+1)$ which becomes small as the number of sites N increases. Thus, we can write the exciton energy fluctuations as

$$\delta E(t) \approx \frac{2|J|}{\ell^2}\delta k(t). \tag{11}$$

This model assumes that the exciton is in some thermal population driven by contact with a finite temperature bath, which is. left unspecified. We can use the fluctuation/dissipation theorem,

$$\langle \delta E(t)\delta E(0)\rangle \propto k_B T \frac{2|J|}{\ell^2} Z(t), \tag{12}$$

where the memory kernel $Z(t)$ is the Fourier transform of the spectral density associated with the system/bath interaction. [7][8]

Consequently, the homogeneous lineshape is expected to increase with temperature. Both of these trends are apparent in Refs. [4][5]

However, this model is also unsatisfactory since it imposes a localization length, ℓ, on the exciton and does not account for lattice reorganization effects which would contract the exciton and would suggest that the homogeneous linewidths of the photoemission spectra would be broad compared to the absorption spectra. This prompts us to consider a unified model under which the coupling between the lattice and the exciton is treated under a non-perturbative and self-consistent framework at both $T = 0K$ and at finite temperature.

B. Self-trapped excitons

We seek a non–perturbative approach whereby the lattice relaxation and the exciton are treated on co-equal footings. black

A suitable starting point is the Holstein model where by the phonon variables $[a_{n'}, a_n^\dagger] = \delta_{nn'}$ are taken to be local to each electronic site:

$$H_{lat} + H_{int} = \sum_n \hbar\omega a_n^\dagger a_n + \sum_n \chi(a_n^\dagger + a_n)|n\rangle\langle n| \qquad (13)$$

Writing the exciton wavefunction as

$$|\psi\rangle = \sum_n \phi_n |n\rangle \qquad (14)$$

and then minimization of the energy $E = \langle\psi|H\psi\rangle$ with respect to the

phonons, and treating them as c–number variables as per the Ehrenfest approximation, one easily finds $a_n = -\chi|\phi_n|^2$. Substituting this back into energy expectation value, leads to the discrete non–linear Schrödinger equation

$$i\hbar\dot{\phi}_n = E_n\phi_n + J(\phi_{n+1} + \phi_{n-1}) - \frac{2\chi^2}{\hbar\omega}|\phi_n|^2\phi_n \qquad (15)$$

which has been used extensively for modeling problems such as this. [9]

Finally, the discrete lattice model can be taken in the long–wavelength/semiclassical limit and one arrives at a non–linear Schrödinger equation (NLS) of the form [10]

$$i\hbar\partial_t\phi = \left(-J\nabla^2 - g|\phi|^2 - E_o)\right)\phi \qquad (16)$$

with non–linearity $g = 2\chi^2/\hbar\omega$.

Eqs. 16 and 15 are formally equivalent in the limit that $N \to \infty$ and the lattice constant goes to 0. The NLSE has localized solutions when $g > 0$,

$$\phi(x) = \sqrt{\frac{1}{2\lambda}}\frac{1}{\cosh(x/\lambda)}, \qquad (17)$$

in which the exciton is localized over a finite spatial region with eigenvalue $\mu = -g^2/16J$ and $\lambda = 4J/g$. The $|\phi(x)|^2$ solution acts as a self-trapping potential

$$V(x) = \sqrt{\frac{g^2}{2\lambda}}\frac{1}{\cosh(x/\lambda)} \qquad (18)$$

which is the well-known Pöschel-Teller potential. [11]

It is important to note that this system as a single bound state.

We can now directly relate the parameters of our model to observed spectroscopic quantities. The reorganization energy can be conveniently deduced from the exciton photoluminescence spectrum via the Huang-Rhys parameter, S and phonon frequency Ω

$$E_{reorg} = \hbar\Omega S. \tag{19}$$

Equating the two expressions,

$$T^* = 18\hbar\Omega S/k_B \tag{20}$$

which for typical conjugated polymer systems, $S \approx 1$ and $\hbar\Omega \approx 200 meV$ giving indicating that we are comfortably in the extreme low-temperature regime of the model for excitons localized to single chains. However, for J-aggregate systems in which the electronic coupling is distributed over multiple chromophores the critical temperature can be considerably than in the isolated chain case; however, even in the most extreme cases $T \ll T^*$ implying that the model should be valid for a wide range of organic-semiconducting materials.

Lastly, we can compute the inverse participation ratio (IPR) directly from the STE state,

$$IPR = \int_{-\infty}^{\infty} dx |\phi(x)|^4 = \frac{1}{3\lambda} = \frac{g}{12J} \tag{21}$$

This expression reveals how exciton delocalization which increases with J and exciton/phonon coupling, which localizes the state compete to determine the exciton localization length.

C. STE Homogeneous linewidth

We assume that dynamical fluctuations correspond to excitations from the STE state and that these give rise to the homogeneous line width of the exciton.

$$\sigma_E^2 = \langle (E - \langle E \rangle^2 \rangle \tag{22}$$

which we can evelute analytically by defining the partition function

$$
\begin{aligned}
Z &= e^{\beta\mu} \sum_{k=0}^{\infty} e^{-J\beta k^2} \\
&= \frac{1}{2} e^{\beta\mu} \left(\vartheta_3 \left(0, e^{-J\beta} \right) + 1 \right) \\
&= e^{\beta\mu} (1 + e^{-\beta J} + e^{-4\beta J} + \cdots)
\end{aligned}
\tag{23}
$$

where $\vartheta_n(0, q)$ is the

elliptic theta function which we approximate as a series

at low temperature ($q = e^{-\beta J} \ll 1$)

$$\vartheta_n(0, q) = 1 + 2q + 2q^4 + \mathcal{O}[q]^6.\tag{24}$$

This gives the low temperature limit for the line width as

$$\sigma_E^2 = \frac{J^2 e^{3\beta J}\left(16 e^{\beta J} + e^{4\beta J} + 9\right)}{\left(e^{3\beta J} + e^{4\beta J} + 1\right)^2}\tag{25}$$

At high temperature, the sum can be taken as integral

$$Z \to \frac{e^{\mu\beta}}{2\beta}\tag{26}$$

and

$$\sigma_E^2 = \frac{1}{\beta^2}.\tag{27}$$

In Fig. 1 we show the homogeneous line width vs. temperature plotted in physical units over a range of exciton reorganization energies using the exact expression obtained from Eq. 23, These have a general characteristic of being independent of temperature up to an activation temperature characteristic of the exciton reorganization energy, after which the line width increases monotonically. At temperatures just above the activation temperature, the behaviour is nearly linear. This model seamlessly connects the trends are apparent in Refs. [4][5] for excitons in 1D.
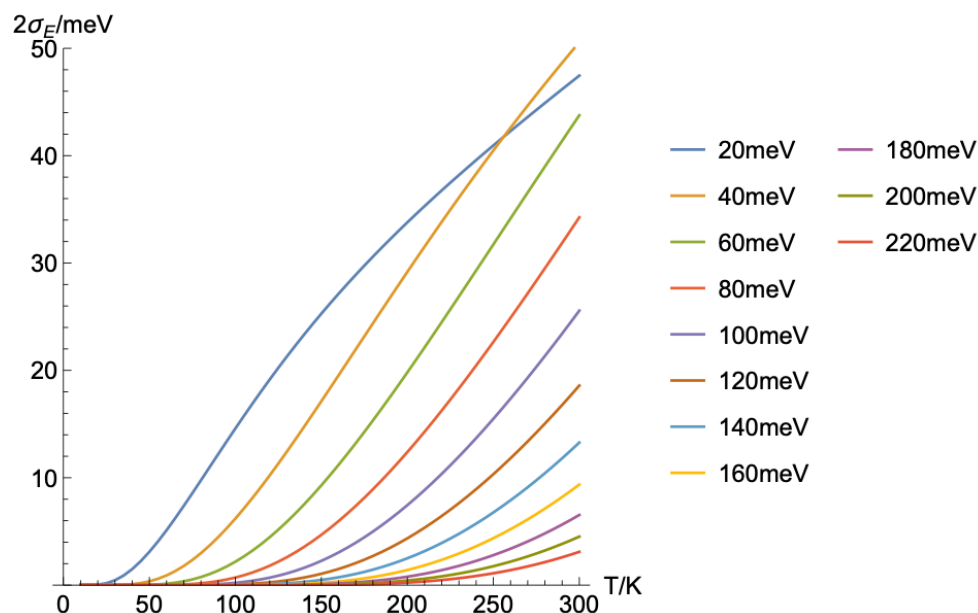
Figure 1. Energy variance vs temperature over a range of exciton reorganization energies. This quantity corresponds to the additional homogeneous width of the transition accounting for the thermal fluctuations in the exciton energy.

III. Discussion

Elementary quantum mechanics guarantees that every purely attractive potential in one-dimension has at least a single bound state. In conjugated polymer and molecular aggregates this corresponds to a localized excitonic state dressed by the self-consistent reorganization of the molecular lattice about the state. Self-consistent excitations from this state arising from thermal excitations destabilize the state and lead to a contribution to the exciton's optical lineshape.

Our calculations and analysis reveal that for systems with strong exciton/phonon coupling, such as polymer aggregates, the exciton homogeneous line width is for the most part independent of the temperature for $T \ll \hbar\mu/k$; however, for molecular J-aggregates which exhibit much weaker exciton/phonon coupling one expects a monotonic and nearly linear increase in the line width that can be well-approximated within the exchange narrowing model.

It would be of interest to apply the analysis to other polaron models, such as the Su-Schrieffer-Heeger model [12] which has direct bearing on topological soliton states [13], topological insulators, and one-

dimensional optomechanical arrays. [14]

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Data Availability

The data that supports the findings of this study are available within the article.

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Declarations

Potential competing interests: No potential competing interests to declare.