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INHOMOGENEOUS BROADENING IN EXCITONIC SYSTEMS

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The effect of a random distribution of single-center transition frequencies on the spectrum of a system whose optically active states are Frenkel excitons is addressed from a theoretical perspective. In the weak disorder limit (distribution width/exciton bandwidth $\ll 1$), the lineshape is adequately described by a theory based on the coherent potential approximation (CPA) in all three dimensions. The theory is shown to account quantitatively for recent numerical results for the linewidth in one dimensional arrays reported by Köhler et al. In the strong disorder limit (distribution width/exciton bandwidth $\gg 1$), a theory is outlined in which the inter-center coupling is treated as a perturbation. The resulting lineshape has a Voigt profile. The need for a theory interpolating between the weak disorder and strong disorder limits is pointed out.

1. Introduction

The purpose of this paper is to give a brief overview of the theory of the effects of inhomogeneous broadening on the optical spectra of systems whose excited states are Frenkel excitons. The Hamiltonian associated with such systems takes the form

$$\mathscr{H} = \sum_j V_j a_j^+ a_j + \sum_{(i,j)} t_{ij}\left(a_i^+ a_j + a_j^+ a_i\right), \tag{1}$$

where the a_i and a_i^+ are the exciton annihilation and creation operators in the site representation, V_j is the single-center transition freqency ($\hbar = 1$), and t_{ij} is the electron transfer integral between lattice sites i and j. In what follows, it will be assumed that the t_{ij} depend only on the relative separation of sites i and j. The transition frequency, V_j, is separated into a site-independent term, V_0, and a site-dependent fluctuation, ΔV_j:

$$V_j = V_0 + \Delta V_j. \tag{2}$$

The ΔV_j, which give rise to the inhomogeneous broadening, are postulated to have a common probability distribution, $P(\Delta V)$, but to be uncorrelated from site to site. With little loss in generality, the assumption is made that $P(\Delta V)$ is symmetric, $P(-\Delta V) = P(\Delta V)$, so that

$$\langle \Delta V \rangle = \int \mathrm{d}\,\Delta V\, P(\Delta V)\, \Delta V = 0. \tag{3}$$

In the absence of inhomogeneous broadening, the eigenstates of the Hamiltonian (1) are labeled by the wavevector $\boldsymbol{k}$ associated with the Brillouin zone of the lattice of active centers. The corresponding energies take the form

$$E_k = V_0 + \sum_j t_{ij} \exp\left[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_i - \boldsymbol{r}_j)\right]. \tag{4}$$

The states involved in sharp line, zero-phonon transitions have $\boldsymbol{k} \approx 0$. We will assume that these states lie at the bottom of the exciton band.

In the analysis of the effects of inhomogeneous broadening on the optical spectrum, the important parameter is the ratio of the width of the distribution of ΔV, denoted by σ ($\sigma^2 = \int \mathrm{d}\,\Delta V P(\Delta V)\,(\Delta V)^2$), to the excition bandwidth, W. When $\sigma/W \ll 1$, one can treat the distribution of the ΔV_i as a perturbation on the ideal excitonic system. In the opposite limit, it is the coupling t_{ij} which perturbs the array of independent centers [1,2].

In the weak disorder limit, $\sigma/W \ll 1$, the effect of the inhomogeneities is to shift and broaden the exciton line. The shift in the optical transition frequency, $\Delta\omega$, can be calculated from second order perturbation theory, with the result [3]

$$\Delta\omega = \sigma^2 N^{-1} \sum_k \left[E_0 - E_k\right]^{-1}, \tag{5}$$

where N is the number of centers. To order σ^2, the half width at half maximum, Γ, is given by the 'golden rule' expression [3]

$$\Gamma = \pi\sigma^2 N^{-1} \sum_k \delta(E_0 - E_k). \tag{6}$$

Since $E_k - E_0 \approx Dk^2$ for small k, the second order shift is finite in three dimensions but diverges in one and two dimensions. Furthermore, according to eq. (6), in three

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dimensions, Γ vanishes to order σ^2, whereas it is finite in two dimensions and divergent in one dimension.

2. Coherent potential approximation

The failure of second order perturbation theory to give finite results for the lineshift in less than three dimensions points out the need for an alternative approach to the calculation of the optical lineshape. Such an approach is provided by the coherent potential approximation or CPA [4–6]. In the CPA, the lineshape is given by an expression of the form

$$\rho(E) = \frac{\operatorname{Im} V_c(E)/\pi}{(E - \operatorname{Re} V_c(E))^2 + (\operatorname{Im} V_c(E))^2}. \tag{7}$$

Here Re V_c and Im V_c are the real and imaginary parts of the coherent potential, which is obtained as the solution to the equation

$$\int \mathrm{d}\,\Delta V \frac{P(\Delta V)[\Delta V - V_c(E)]}{1 - (\Delta V - V_c(E)) g_{00}[E - V_c(E)]} = 0, \tag{8}$$

where g_{00} is given by

$$g_{00}(E) = N^{-1} \sum_k [E + E_0 - E_k]^{-1}, \tag{9}$$

in which E_k and E_0 are obtained from eq. (4) (Note that the zero of energy is taken to be the bottom of the unperturbed exciton band.)

Even at the band edge ($E = 0$), a solution to eq. (8) can only be obtained by numerical methods. However, in the limit $\sigma/W \to 0$, one can expand the denominator in powers of $(\Delta V - V_c)g_{00}$ and obtain

$$V_c(E) = \sigma^2 g_{00}[E - V_c(E)]. \tag{10}$$

In this limit, the line shape is approximately Lorentzian, with a shift and halfwidth, Re $V_c(0)$ and Im $V_c(0)$, respectively.

The values obtained for $V_c(0)$ depend on the dimensionality of the system. In three dimensions, $g_{00}(0)$ is finite and real. Im $V_c(0)$ is zero (to order σ^2) and Re $V_c(0)$ is identical to the second order perturbation result, eq. (5). In two dimensions, care must be taken in the limit $E \to 0$. Writing g_{00} as an integral over k and using the long wavelength approximation for E_k, $E_0 + Dk^2$, one has

$$g_{00}(-V_c) = -(A/N)(4\pi D)^{-1} \int_0^c \frac{\mathrm{d}u}{V_c + u}, \tag{11}$$

where A is the area of the system and c is a Debye-like cutoff to the integral. Using the symbolic identity $(x + \mathrm{i}\epsilon)^{-1} = \mathscr{P}/x - \mathrm{i}\pi\delta(x)$, $\mathscr{P}$ denoting the principal value, and identifying ϵ with Im V_c, we obtain the equations

$$\operatorname{Im} V_c(0) = \Gamma = \sigma^2 (A/4DN), \tag{12}$$

and

$$\operatorname{Re} V_c(0) = -\sigma^2 (A/4\pi DN) \mathscr{P} \int_0^c \frac{\mathrm{d}u}{u + \operatorname{Re} V_c(0)}. \tag{13}$$

Eq. (11) yields a linewidth identical to that given by the golden rule, eq. (6). The solution to eq. (13) is sightly more complicated. Evaluating the integral one obtains the result

$$\operatorname{Re} V_c(0) = X \ln(c/|\operatorname{Re} V_c(0)|), \tag{14}$$

where

$$X = \sigma^2 (A/4\pi DN). \tag{15}$$

In the limit as $X \to 0$, the solution to (14) is increasingly well approximated by

$$\operatorname{Re} V_c(0) = \Delta\omega = -X \ln(c/X), \tag{16}$$

which shows that the line shift vanishes somewhat less rapidly than the linewidth.

The behaviour in one dimension is even more unusual. This is brought out in a calculation for a one dimensional array with nearest-neighbor interactions. In such a system, g_{00} is given by

$$g_{00}(E - V_c) = [(E - V_c)(E - V_c - 4t)]^{-1/2}, \tag{17}$$

for a bandwidth equal to $4t$. The resulting equation for V_c takes the form

$$V_c^{3/2} = \sigma^2/(4t)^{1/2}. \tag{18}$$

A detailed analysis shows that the complex root

$$V_c = \sigma^{4/3}(4t)^{-1/3} \exp[8\pi\mathrm{i}/3], \tag{19}$$

is the one that matches the numerical solution of the general equation. From (19) one has

$$\operatorname{Re} V_c(0) = \Delta\omega = -Y/2, \tag{20a}$$

$$\operatorname{Im} V_c(0) = \Gamma = \sqrt{3}\, Y/2, \tag{20b}$$

where

$$Y = \sigma^{4/3}(4t)^{-1/3}, \tag{21}$$

from which it is evident that both the lineshift and linewidth vanish at the same rate, in contrast to what is found in higher dimensions.

The variation of the linewidth and lineshift in the CPA contrasts with the results of the average t-matrix approximation, or ATA [7], which reduces to second order perturbation theory in the weak disorder limit, and thus breaks down below three dimensions.

3. Strong disorder limit

The CPA approach outlined in the preceding section becomes less accurate with increasing values of the ratio σ/W. Insight into the behavior in the regime $\sigma/W \gg 1$ can be obtained from a calculation in which the coupling between the centers is treated as a perturbation. In this approach, the lineshape is expressed as a convolution of the distribution of the Δv with the single-center lineshape function, viz.

$$\rho(E)=C\int P(E-V_0-y)I(y)\,\mathrm{d}y, \tag{22}$$

where C is a constant and $I(y)$ is the lineshape function for a center with transition frequency V_0+y.

When there is no interaction between the centers, $I(y)=\delta(y)$, neglecting homogeneous linebroadening. In lowest order , the effect of the interactions on the ith center can be included by introducing a self energy of the form

$$X_i=\sum_j \frac{|t_{ij}|^2}{E_i-E_j+\mathrm{i}\epsilon}, \tag{23}$$

where $E_i=V_0+\Delta V_i$. In what follows, we will assume that for each value of $|t_{ij}|^2$, there are many sites that contribute to the sum (many neighbor approximation). In this limit the sum over j can be approximated according to

$$\sum_j \frac{|t_{ij}|^2}{E_i-E_j+i\epsilon}\to T^2\int\frac{\mathrm{d}u\,P(u)}{\Delta V_i-u+\mathrm{i}\epsilon}, \tag{24}$$

where $T^2=\sum_j|t_{ij}|^2$.

Using the symbolic identity for $(x+\mathrm{i}\epsilon)^{-1}$ mentioned previously, the self energy becomes

$$X(\Delta V_i)=T^2\left(\mathscr{P}\int\frac{\mathrm{d}u\,P(u)}{\Delta V_i-u}-\mathrm{i}\pi P(\Delta V_i)\right), \tag{25}$$

where $\mathscr{P}$ refers to the principal value. The corresponding lineshape function takes the form

$$\begin{aligned} I(y)&=\frac{\operatorname{Im}X(y)/\pi}{(y-\operatorname{Re}X(y))^2+(\operatorname{Im}X(y))^2},\\ &=\frac{T^2P(y)}{\left(y-T^2\mathscr{P}\int\frac{\mathrm{d}u\,P(u)}{y-u}\right)^2+\left(\pi T^2P(y)\right)^2}. \end{aligned} \tag{26}$$

A Lorentzian approximation to the single-center lineshape is obtained by using the form appropriate to small y, $|y|\ll\sigma$, which is the important regime when $\sigma/W\gg1$. One has

$$I(y)=\frac{T^2P(0)}{y^2\left(1+T^2\int(\mathrm{d}P/\mathrm{d}v)v^{-1}\,\mathrm{d}v\right)^2+\left(\pi T^2P(0)\right)^2}, \tag{27}$$

having approximated the principal value integral according to

$$\begin{aligned} \mathscr{P}\int\frac{\mathrm{d}u\,P(u)}{y-u}&=-\mathscr{P}\int\frac{P(v+y)\,\mathrm{d}v}{v}\\ &\approx -y\int(\mathrm{d}P(v)/\mathrm{d}v)v^{-1}\,\mathrm{d}v+O(y^3), \end{aligned} \tag{28}$$

as is appropriate for a symmetric distribution. The convolution of the Lorentzian single-center lineshape with the distribution of transition frequencies leads to a generalized Voigt profile that becomes the traditional Voigt profile when P is a gaussian,

$$P(\Delta V)=(2\pi\sigma^2)^{-1/2}\exp\left[-(\Delta V)^2/2\sigma^2\right].$$

In this case, one finds

$$I(y)=\frac{T^2/(2\pi\sigma^2)^{1/2}}{y^2(1-T^2/\sigma^2)^2+\left(T^2(\pi/2\sigma^2)^{1/2}\right)^2}, \tag{29}$$

for the lineshape.

4. Discussion

In §2 the point was made that even in the weak disorder regime, $\sigma/W\ll1$, second order perturbation theory gave divergent results for the lineshift in less than three dimensions. The failure of perturbation theory (and the average t-matrix approximation) was remedied by the coherent potential approximation which reproduces the results of perturbation theory in three dimensions and gave finite results for the lineshift and linewidth in lower dimensions. The numerical data for the linewidth reported in ref. [3] are consistent with the results for the linewidth obtained from eq. (9) in the sense that the linewidth varies more rapidly than σ^2 in three dimensions, is proportional to σ^2 in two dimensions, and vanishes as $\sigma^{4/3}$ in one dimension. Accurate numerical data for the linewidth in one dimension are presented in ref. [8] for a gaussian distribution in ΔV. The authors find that the full width at half maximum is given by

$$\mathrm{FWHM}=1.2(\sigma/t)^{4/3}t, \tag{30}$$

which differs by less than ten per cent from the CPA value

$$2\Gamma=1.1(\sigma/t)^{4/3}t. \tag{31}$$

The situation with respect to the lineshift is not as clear. The authors of ref. [3] claim their lineshift data are compatible with $\Delta\omega$ being proportional to σ^2. However, the data they display show a less rapid variation in one and two dimensions, qualitatively consistent with predictions of the CPA. Further numerical analysis, at the level of accuracy of ref. [8], is needed to test the predictions of the CPA for the lineshift in one dimension.

The pronounced difference in the expressions for the lineshape in the weak disorder, $\sigma/W\ll1$, and the strong disorder, $\sigma/W\gg1$, regimes is striking. The progressive breakdown of the CPA with increasing disorder [6] points out the need for a theory for the lineshape, valid in all dimensions, which interpolates between the

CPA and the approximate treatment for the strong disorder limit outlined in §3.

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Note added in proof. The lineshift for a one dimensional array with 10^6 sites has been calculated using the approach outlined in ref. [8]. Quantitative agreement with the predictions of the CPA (eq. 20a) is obtained for $(\sigma/t)^{4/3} \leq 0.1$ (J. Köhler, private communication). Also, the linewidth in three dimensions has been evaluated in the CPA using an approximate greens function appropriate for a simple cubic lattice with nearest-neighbor interactions. The width was found to vary as σ^3 for small σ, in agreement with the numerical results of ref. [3].

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