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Decay of the $\vec{k} = 0$ exciton mode at a finite trap concentration

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We study the decay of the $\vec{k} = 0$ exciton mode in the presence of a finite concentration of traps. It is assumed that the traps are distributed at random and that each trap can couple to a single donor. Particular attention is paid to the behavior of one- and two-dimensional systems where algebraic decay was predicted on the basis of the average T-matrix approximation (ATA). Using the coherent potential approximation (CPA), we find that the ATA and CPA give similar results at all times in three-dimensional systems with a low concentration of traps. In one- and two-dimensional systems the ATA and CPA agree at short times, while at long times the CPA predicts exponential decay with a complex decay rate. The variation of the decay rate with trap concentration is determined in the low-concentration limit.

I. INTRODUCTION

In a recent paper[1] we studied the decay of the fluorescence in a system where the transfer of excitation between optically excited donor ions took place coherently. It was assumed that there was a small concentration of trapping centers (acceptors) distributed at random. Transfer to the traps was a one-way (on the time scale of interest) incoherent process involving the emission of a phonon. The configurational average of the probability amplitude characterizing the decay of a eigenstate of the donor array (a Frenkel exciton) was calculated treating the trapping in the average T-matrix approximation (ATA).

In the analysis of the decay of the uniform mode ($\vec{k} = 0$ exciton) in a donor array with translational symmetry, anomalous behavior was obtained in one- and two-dimensional systems. In contrast to three-dimensional systems, where the asymptotic decay of the probability amplitude was exponential, the probability amplitude in one and two dimensions decayed as $t^{-1/2}$ and t^{-1}, respectively. The source of these anomalies was traced to the singular behavior of the unperturbed donor Green's function

$$g_0(E) = \frac{1}{N}\sum_{\vec{k}}(E - E_{\vec{k}})^{-1} \quad , \tag{1.1}$$

in which N is the number of donors, $E_{\vec{k}}$ denotes the energy of a donor exciton with wave vector $\vec{k}$, and the sum is over the appropriate Brillouin zone. In one and two dimensions $g_0(E)$ diverges as $(E - E_0)^{-1/2}$ and $\ln(E - E_0)$, respectively.[2]

The algebraic decay of the probability amplitude at low dimensions is analogous to the algebraic decay of the total number of excited donors in one- and two-dimensional systems which was obtained for the incoherent donor-donor transfer problem in the ATA.[3,4] Recently it was found that the number of excited donors calculated in the coherent potential approximation (CPA) behaves quite differently below three dimensions[5]. The CPA results for the number of excited donors agreed with the ATA at short times. However, at long times there was a crossover into exponential decay, analogous to three dimensions. But unlike three dimensions the decay rates were nonlinear functions of the trap concentration varying as c_A^2 (one dimension) and $c_A/|\ln c_A|$ (two dimensions) in the limit as c_A, the probability of a donor site being associated with a trap, $\rightarrow 0$. Comparison with exact results, which are available for a one-dimensional system with incoherent donor-donor transfer and infinitely fast, zero-range donor-trap transfer,[6] indicates that the CPA result, while not exact, is significantly better than that obtained with the ATA.

Because of the probable superiority of the CPA over the ATA it is worthwhile to apply the CPA formalism to the trapping of excitation in systems with coherent donor-donor transfer. This note is the report of such an analysis. As in Ref. 5 we study a simplified model where it is assumed that each trap interacts with a single donor. We also assume near-neighbor donor-donor interactions so that the (Frenkel) excitation energy takes the form ($\hbar = 1$)

$$E_{\vec{k}} = J{\sum_{j}}' e^{i\vec{k}\cdot\vec{r}_{ij}} \ , \tag{1.2}$$

where the sum on j is over the z nearest neighbors of site i.

In the ATA the configurational average of the probability amplitude of the $\vec{k} = 0$ mode, $\langle R_0(t)\rangle_c$, takes the form

$$\langle R_0(t)\rangle_c = \left[\frac{i}{2\pi}\right] \times \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}[\omega + i\epsilon - E_0 + X_{\text{ATA}}(\omega + i\epsilon)]^{-1} \ , \tag{1.3}$$

where the self-energy in the ATA is given by

$$X_{\text{ATA}}(E) = \frac{ic_A\gamma}{1 + i\gamma g_0(E)} \ , \tag{1.4}$$

with γ denoting the (single) donor-trap transfer rate. In Sec. II we indicate how $\langle R_0(t)\rangle_c$ is modified when the CPA self-energy is used in place of $X_{\text{ATA}}(E)$.

II. CPA

A. General formulation

The development of the CPA for the coherent transfer problem proceeds in a manner analogous to the formulation of the CPA for incoherent donor-donor transfer.[5] In place of X_{ATA} in (1.3) we have X_{CPA}, where X_{CPA} is a solution to the equation

$$\int \frac{d\gamma P(\gamma)[i\hat{\gamma} - X_{\text{CPA}}(E)]}{1 + [i\hat{\gamma} - X_{\text{CPA}}(E)]G_0(E)} = 0 \ . \tag{2.1}$$

Here $P(\hat{\gamma})$ is the probability distribution for the random variable $\hat{\gamma}$ characterizing the donor-trap transfer. For the model under consideration we have

$$P(\hat{\gamma}) = c_A\delta(\hat{\gamma} - \gamma) + (1 - c_A)\delta(\hat{\gamma}) \ . \tag{2.2}$$

The Green's function appearing in Eq. (2.1) is given by an expression similar to (1.1)

$$G_0(E) = \frac{1}{N}\sum_{\vec{k}}[E + X_{\text{CPA}}(E) - E_{\vec{k}}]^{-1} \ . \tag{2.3}$$

With the distribution (2.2) Eq. (2.1) reduces to

$$X_{\text{CPA}} = \tfrac{1}{2}\{ Q + i\gamma - [(Q + i\gamma)^2 - 4ic_A\gamma Q]^{1/2} \} \tag{2.4}$$

where

$$Q = 1/G_0(E) \ . \tag{2.5}$$

When $c_A << 1$ Eq. (2.4) becomes

$$X_{\text{CPA}}(E) = \frac{ic_A\gamma}{1 + i\gamma G_0(E)} \ , \tag{2.6}$$

which is equivalent to (1.4) with g_0 replaced by G_0.

In the opposite limit, $c_A = 1$, we have

$$X_{\text{CPA}}(E) = i\gamma \ , \tag{2.7}$$

which is to be expected since in this limit all donors have traps associated with them. Under these conditions donor-donor transfer has no influence on the rate of transfer to traps.[5]

Our primary interest in this paper is in the asymptotic behavior of $\langle R_0(t)\rangle_c$ when $c_A << 1$. In the case of three-dimensional arrays, where $g_0(E_0)$ is finite, it is sufficient to approximate $X_{\text{CPA}}(E)$ by $X_{\text{ATA}}(E_0)$ in determining the asymptotic behavior. We obtain the result[1]

$$\langle R_0(t)\rangle_c = e^{-iE_0t}\exp\{ ic_A\gamma^2 g_0(E_0)t/[1 + \gamma^2 g_0^2(E_0)] - c_A\gamma t/[1 + \gamma^2 g_0^2(E_0)] \} \ , \tag{2.8}$$

valid when $c_A << 1$.

B. One and two dimensions

In analyzing the asymptotic behavior of $\langle R_0(t)\rangle_c$ in one and two dimensions it is convenient to measure energies relative to E_0. Writing $\hat{E} = E - E_0$ we approximate $\langle R_0(t)\rangle_c$ by expanding X_{CPA} about E_0, viz.

$$\langle R_0(t)\rangle_c = \left[\frac{i}{2\pi}\right] e^{-iE_0t}\int \frac{d\hat{E}\, e^{-\hat{i}Et}}{\hat{E} + X_{\text{CPA}}(\hat{E} + E_0)} \simeq \left[\frac{i}{2\pi}\right] e^{-iE_0t}\int \frac{d\hat{E}\, e^{-i\hat{E}t}}{\hat{E} + X_{\text{CPA}}(E_0) + X'_{\text{CPA}}(E_0)\hat{E}} \tag{2.9}$$

where $X'_{\mathrm{CPA}}(E_0) = dX_{\mathrm{CPA}}(E_0)/dE_0$. Evaluating the integral by closing the contour in the lower half plane we obtain the result

$$\langle R_0(t)\rangle_c \sim \frac{e^{-iE_0t}}{1+X'_{\mathrm{CPA}}(E_0)} \exp\left[\frac{iX_{\mathrm{CPA}}(E_0)t}{1+X'_{\mathrm{CPA}}(E_0)}\right] . \tag{2.10}$$

Note that in three dimensions we have $X'_{\mathrm{CPA}}(E_0) \approx X'_{\mathrm{ATA}}(E_0) << 1$ so that (2.10) reduces to (2.8) for $c_A << 1$.

In one dimension $G_0(\hat{E} + E_0)$ is given by[4]

$$G_0(\hat{E} + E_0) = \{ 2J^{1/2}[\hat{E} + X_{\mathrm{CPA}}(E_0 + \hat{E})]^{1/2} \}^{-1} , \tag{2.11}$$

for $\hat{E} + X_{\mathrm{CPA}}(\hat{E} + E_0) << J$. Using (2.11) in (2.6) we obtain the following equation for X_{CPA}:

$$X_{\mathrm{CPA}}(\hat{E} + E_0) = \frac{ic_A\gamma}{1 + (i\gamma/2J^{1/2})[\hat{E} + X_{\mathrm{CPA}}(\hat{E} + E_0)]^{-1/2}} . \tag{2.12}$$

Solving (2.12) for $X_{\mathrm{CPA}}(E_0)$ and $X_{\mathrm{CPA}}(E_0)$ we find

$$X_{\mathrm{CPA}}(E_0) = 4c_A^2J + 32ic_A^3J^2\gamma^{-1} + O(c_A^4) , \tag{2.13}$$

$$X'_{\mathrm{CPA}}(E_0) = 1 + O(c_A) . \tag{2.14}$$

Where $O(c_A^3)$, etc., means terms proportional to the third and higher powers of c_A.

In two dimensions we have[4]

$$G_0(\hat{E} + E_0) = \frac{1}{4\pi J} \ln\{ 32J/[\hat{E} + X_{\mathrm{CPA}}(\hat{E} + E_0)] \} \tag{2.15}$$

for $\hat{E} + X_{\mathrm{CPA}}(\hat{E} + E_0) << J$. The corresponding equation for X_{CPA} becomes

$$X_{\mathrm{CPA}}(\hat{E} + E_0) = \frac{i\gamma c_A}{1 + (i\gamma/4\pi J)\ln\{ 32J/[\hat{E} + X_{\mathrm{CPA}}(\hat{E} + E_0)] \}} \tag{2.16}$$

After introducing the variables $u = X_{\mathrm{CPA}}/32J$, $\tilde{c}_A = \pi c_A/8$, $y = \gamma/4\pi J$, and $x = \hat{E}/32J$, Eq. (2.16) can be written

$$u(x) = \frac{iy\tilde{c}_A}{1 - iy\ln[x + u(x)]} . \tag{2.17}$$

Separating u into real and imaginary parts we find that $\mathrm{Re}\,u(0)$ [$= \mathrm{Re}\,X_{\mathrm{CPA}}(0)/(32J)$] is a solution to the equation

$$\mathrm{Re}\,u(0) = -\tilde{c}_A/\ln[\mathrm{Re}\,u(0)] , \tag{2.18}$$

whereas

$$\begin{aligned} \mathrm{Im}\,u(0) &= \frac{\mathrm{Im}X_{\mathrm{CPA}}(0)}{32J} \\ &= \frac{i\tilde{c}_A}{y\ln^2[\mathrm{Re}\,u(0)]} \end{aligned} \tag{2.19}$$

and

$$\begin{aligned} \frac{du(0)}{dx} &= \frac{dX_{\mathrm{CPA}}(E_0)}{dE_0} \\ &= \frac{\tilde{c}_A}{\mathrm{Re}\,u(0)\ln^2[\mathrm{Re}\,u(0)]} \\ &= -\{ \ln[\mathrm{Re}\,u(0)] \}^{-1} , \end{aligned} \tag{2.20}$$

the last step following from (2.18). Since $\mathrm{Re}\,u(0) \to 0$ as $c_A \to 0$, $du(0)/dx$ vanishes in the same limit. Equations (2.10), (2.13), (2.14), and (2.18)–(2.20) are the principal results of this section. We discuss their implications in Sec. III.

III. DISCUSSION

In one and two dimensions when $c_A << 1$ the ATA and the CPA give comparable values of $\langle R_0(t)\rangle_c$ at short times. However, at long times there is a qualitative difference in the results obtained with the two approximations. As is evident from a comparison of (1.4) and (2.6) the predictions of the two theories will begin to differ when $G_0(\hat{E} + E_0)$ is no longer approximately equal to $g_0(\hat{E} + E_0)$. This will happen when $\hat{E} \approx X_{\mathrm{CPA}}(0)$, or equivalently, at a time on the order of $[\mathrm{Re}X_{\mathrm{CPA}}(0)]^{-1}$. Thus for $0 \leq t << [\mathrm{Re}X_{\mathrm{CPA}}(0)]^{-1}$ the ATA and CPA will give similar results, whereas for $t >> [\mathrm{Re}X_{\mathrm{CPA}}(0)]^{-1}$ the CPA is expected to be the superior approximation.

On the basis of the analysis in Sec. II, $\langle R_0(t)\rangle_c$ in one dimension is predicted to vary as

$$\langle R_0(t)\rangle_c \sim (\tfrac{1}{2})e^{-iE_0t}\exp(2ic_A^2Jt - 16c_A^3J^2\gamma^{-1}t) . \tag{3.1}$$

From (3.1) it is apparent that the interaction with the traps leads to both a shift ($\propto c_A^2$) and a damping ($\propto c_A^3$) of the uniform mode. The origin of the shift, $\Delta E_0 = -2c_A^2 J$, can be understood as follows. In the strong trapping limit, $\gamma/J >> 1$, the effect of the traps is to "deplete" the probability density leading to an effective exciton wave function which has modes at the locations of the traps. The energy of such a state is approximately

$$E_{0\,\mathrm{eff}} = 2J\cos(k_{\mathrm{eff}}a) \ , \tag{3.2}$$

where a is the lattice constant and k_{eff} is an effective wave vector determined by the distance between nodes. We take

$$k_{\mathrm{eff}}L_t = \pi \ , \tag{3.3}$$

where L_t is the average spacing between traps a/c_A. Thus from (3.3) we have

$$k_{\mathrm{eff}} = \pi c_A/a \ , \tag{3.4}$$

so that

$$\Delta E_0 = -J(k_{\mathrm{eff}}a)^2 = -\pi^2 J c_A^2 \ , \tag{3.5}$$

which is the same order of magnitude as the shift shown in (3.1).

There is an analogous shift and damping in higher dimensions as well. In three dimensions both the shift and the damping are proportional to c_A [cf. Eq. (2.8)], whereas in two dimensions we obtain linear behavior with logarithmic corrections [cf. Eqs. (2.18) and (2.19)].

In many respects the decay of the uniform mode resembles the decay of the total number of excited donors in the incoherent transfer problem.[3–5] In place of (2.9) we have an inversion of a Laplace transform

$$f(t) = \frac{1}{2\pi i}\int ds\, e^{st}[s + X_{\mathrm{CPA}}(s)]^{-1} \ , \tag{3.6}$$

where $f(t)$ is the ratio of the number of donors excited at time t to the number excited at $t = 0$ (in the absence of radiative decay). In the case of a donor array with translational symmetry where each trap interacts with a single donor, $X_{\mathrm{CPA}}(s)$ in the limit $c_A << 1$ is given by an equation analogous to (2.6) (Ref. 5)

$$X_{\mathrm{CPA}}(s) = \frac{\gamma c_A}{1 + \gamma G_0(s)} \ , \tag{3.7}$$

where the Green's function for the incoherent transfer problem has the form

$$G_0(s) = \frac{1}{N}\sum_{\vec{k}}[s + X_{\mathrm{CPA}}(s) + W(0) - W(\vec{k})]^{-1} \ . \tag{3.8}$$

Here $W(\vec{k})$ denotes the Fourier transform of the transfer rate between sites i and j:

$$W(\vec{k}) = \sum_j e^{i\vec{k}\cdot\vec{r}_{ij}} W_{ij} \ . \tag{3.9}$$

In the CPA $f(t)$ decays at a rate proportional to c_A when $c_A << 1$, whereas in one and two dimensions it decays as c_A^2 and $c_A/|\ln c_A|$.[5]

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[1] D. L. Huber, Phys. Rev. B 22, 1714 (1980).

[2] Reference 1, Appendix.

[3] D. L. Huber, Phys. Rev. B 20, 2307 (1979).

[4] K. K. Ghosh and D. L. Huber, J. Lumin. 21, 225 (1980).

[5] K. K. Ghosh and D. L. Huber, Phys. Rev. B 23, 4441 (1981). See also D. L. Huber, Phys. Rev. B. 20, 5333 (1979).

[6] B. Movaghar and G. W. Sauer (unpublished).