Fluorescence in the presence of traps. II. Coherent transfer

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A study is made of the time dependence of the donor fluorescence in a system where there is a small concentration of randomly distributed acceptor ions which act as traps for the excitation. It is assumed that the donor-donor transfer is coherent and that the donor-acceptor transfer is a one-way process involving the emission of a phonon. The probability amplitude characterizing the decay of an eigenstate of the donor array is calculated in the average t-matrix approximation. Both ordered and disordered donor arrays are treated. In the case of the former the decay of the amplitude of the $k=0$ mode is studied in detail. It is found that the decay is exponential in three dimensions and varies as $t^{-1/2}$ and t^{-1} in one and two dimensions, respectively. In disordered systems the distinction is made between extended and localized modes. Approximate calculations appropriate to dilute arrays, which interpolate between these limits, are discussed. The analysis sheds light on the applicability of the Born approximation for the t matrix in both ordered and disordered systems and on the use of fluorescence experiments to detect the existence of a mobility edge between localized and delocalized states in a disordered system.

I. INTRODUCTION

In a recent paper[1] (hereafter referred to as I) we outlined a theory of the fluorescence in a system with a small concentration of impurities which act as traps or acceptors for the excitation. It was assumed that a fraction of the donor ions was excited by a broad-band pulse. The time dependence of the donor fluorescence was calculated for a situation where the excitation could be transferred among the donors as well as from the donors to the traps. The competition between these two processes gave rise to decay rates which depended on the relative magnitudes of the donor-donor and donor-acceptor transfer rates.

The starting point in I was a set of coupled rate equations for the functions $P_n(t)$ characterizing the probability that ion n is excited at time t, all other donors being in the ground state. For a description in terms of rate equations to be appropriate, it is necessary that both the donor-donor and donor-acceptor transfer processes be incoherent, as will be the case when they involve the annihilation and creation of phonons.

In this paper we develop a theory of the fluorescence in the presence of traps which is complementary to I. Instead of incoherent donor-donor transfer, we assume completely coherent transfer among donors. Like I it is applicable when there is a small concentration of traps. Transfer to the traps, which are distributed at random, is accompanied by the spontaneous emission of a phonon and hence is an incoherent process. It is further assumed that the trap depths are much greater than k_BT so that backtransfer is unimportant on the time scale of interest.

Since we are assuming coherent transfer it is necessary to begin with the microscopic Hamiltonian. We use the tight-binding formalism to characterize the donor array. The donor Hamiltonian thus has the form

$$\mathcal{H}_D=\sum_{j=1}^{N}E_jb_j^\dagger b_j+\tfrac{1}{2}\sum_{j\neq l}W_{jl}(b_j^\dagger b_l+b_l^\dagger b_j)\ , \tag{1.1}$$

where E_j is the diagonal energy of the jth donor, N is the number of donors, and W_{jl} denotes the transfer term connecting donors j and l. We assume W_{jl} is both real and symmetric ($W_{jl}^*=W_{jl}=W_{lj}$). The symbols b_j and $b_j^\dagger$ denote annihilation and creation operators, respectively, for the jth donor. They obey the standard Fermi commutation relations.

The Hamiltonian (1.1) can be diagonalized by a unitary transformation. The resulting expression takes the form

$$\mathcal{H}_D=\sum_{\alpha=1}^{N}\epsilon_\alpha c_\alpha^\dagger c_\alpha\ , \tag{1.2}$$

where c_α and $c_\alpha^\dagger$ are the annihilation and creation operators of the αth mode. They are related to the b_j and $b_j^\dagger$ by means of the equations

$$c_\alpha=\sum_j X_{\alpha j}b_j\ , \tag{1.3a}$$

$$c_\alpha^\dagger=\sum_j X_{\alpha j}^*b_j^\dagger\ , \tag{1.3b}$$

$$b_j=\sum_\alpha X_{\alpha j}^*c_\alpha\ , \tag{1.3c}$$

$$b_j^\dagger=\sum_\alpha X_{\alpha j}c_\alpha^\dagger\ . \tag{1.3d}$$

The elements of the $N\times N$ unitary matrix X satisfy the relations

$$\sum_j X_{\alpha j}X_{\alpha' j}^*=\delta_{\alpha\alpha'}\ , \tag{1.4a}$$

$$\sum_\alpha X_{\alpha j}X_{\alpha j'}^*=\delta_{jj'}\ . \tag{1.4b}$$

There is an important comment to be made in connection with Eqs. (1.1)–(1.4). At no point have we made the assumption that the donor array has translational symmetry. Thus the Hamiltonian is appropriate when donors are distributed at random as well as when they form a lattice. Also, we choose to refer to the eigenstates of $\mathcal{H}_D$ as (Frenkel) excitons even though in the case of disordered systems a characterization in terms of wave vector may not be appropriate.

The Hamiltonian associated with the traps is written

$$\mathcal{H}_T = \sum_\mu W_\mu d_\mu^\dagger d_\mu \,, \tag{1.5}$$

where W_μ is the trap energy and d_μ and $d_\mu^\dagger$ are the corresponding annihilation and creation operators. Consistent with the neglect of backtransfer we assume $\mathcal{E}_\alpha - W_\mu \gg k_B T$; all α, μ. The phonon Hamiltonian has the form

$$\mathcal{H}_P = \sum_q \omega_q a_q^\dagger a_q \,. \tag{1.6}$$

Here ω_q is the phonon energy ($\hbar = 1$) and a_q and $a_q^\dagger$ are the (boson) annihilation and creation operators for the mode q where q corresponds to the wave vector and/or other quantum numbers labeling the eigenstates. It should be emphasized that our use of the fermion formalism to describe the donor system and the traps is merely a matter of taste. Since we will be considering only states with zero or one exciton we could equally well have used a boson formalism or dispensed with second quantization entirely.

As mentioned earlier we assume that the transfer of excitation to a trap is accompanied by the emission of a phonon of energy $\epsilon_\alpha - W_\mu$. The Hamiltonian associated with this process is written

$$\mathcal{H}_I = \sum_\mu \sum_j \sum_q [A_{\mu j}(q) a_q^\dagger d_\mu^\dagger b_j + A_{\mu j}^*(q) b_j^\dagger d_\mu a_q] \equiv \sum_\mu h_\mu \,. \tag{1.7}$$

Here $A_{\mu j}(q)$ is the matrix element associated with a process in which excitation is transferred from the jth donor to the μth trap with a phonon q being emitted. By making use of (1.3c) and (1.3d) we can rewrite (1.7) in terms of the normal-mode operators for the excitons:

$$\mathcal{H}_I = \sum_\mu \sum_j \sum_q \sum_\alpha [A_{\mu j}(q) X_{\alpha j}^* a_q^\dagger d_\mu^\dagger c_\alpha + A_{\mu j}^*(q) X_{\alpha j} c_\alpha^\dagger d_\mu a_q] \,. \tag{1.8}$$

It should be mentioned that in writing $\mathcal{H}_I$ we have omitted terms involving $a_q d_\mu^\dagger c_\alpha$ which do not conserve energy in first order and thus have a negligible effect on our results. Moreover, we have not included any terms of the form $(a_q^\dagger + a_q) c_\beta^\dagger c_\alpha$ which scatter excitons from one mode to another. Such effects have been discussed recently by Kenkre[2] and Wong and Kenkre.[3]

As was previously pointed out, it was assumed in I that the initial state of the system corresponded to exciting a small fraction of the donors chosen at random. Such a state can be created by means of optical absorption by using a weak pulsed source whose bandwidth is much greater than the inhomogeneous linewidth. In the present analysis we consider a somewhat different situation. It is assumed that an exciton is created in mode α at $t = 0$. We then calculate the probability amplitude for this state at a later time t. Apart from an exponential factor associated with radiative decay, which we will consistently omit, this amplitude is given by

$$R_\alpha(t) = \langle \alpha | \exp(-i\mathcal{H}t) | \alpha \rangle \,, \tag{1.9}$$

where $|\alpha\rangle$ denotes the one exciton state and $\mathcal{H}$ is the full Hamiltonian $\mathcal{H}_D + \mathcal{H}_T + \mathcal{H}_P + \mathcal{H}_I$.

The experimental situation corresponding to (1.9) can be created optically by using a pulsed source whose bandwidth is much less than the width of the exciton band. When there is translational symmetry the selection rules governing optical absorption permit only exciton modes with wave vectors $\vec{k} \approx 0$ to be created in a direct process. In contrast, in disordered systems where the wave vector is generally not a good quantum number it is usually possible to create excitons at any point in the band.

In Secs. II–IV we will develop a theory for the probability amplitude averaged over all trap configurations, which is applicable whenever the number of traps is much less than the number of donors. Our results are discussed in Sec. V where we consider the connection between the configurational average of the probability amplitude and the measured fluorescent intensity.

II. t-MATRIX ANALYSIS

In this section we will outline a formal calculation of the configurational average of the probability amplitude which is based on the average t-matrix approach.[4] We consider a system which consists of N donors and $N_T (\ll N)$ traps. In damping calculations such as the one outlined here it is useful to consider the operator $G(E) = (E - \mathcal{H})^{-1}$. We restrict our attention to the states $|\alpha\rangle$, $|\beta\rangle$, ... which have one exciton in mode $\alpha, \beta, \ldots$, zero phonons and no excited traps, and the states $|\mu; q\rangle$, $|\mu; q'\rangle, \ldots$ which have no excitons, trap μ excited and one phonon present in mode $q, q', \ldots$.

For $t \geq 0$ the configurational average of the probability amplitude can be written

$$\langle R_\alpha(t)\rangle_c=\frac{i}{2\pi}\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t}\langle\langle\alpha|G(\omega+i\epsilon)|\alpha\rangle\rangle_c\,, \qquad (2.1)$$

where $\langle\cdots\rangle_c$ denotes an average over all configurations of N_T traps. It should be emphasized that $|\langle R_\alpha(t)\rangle_c|^2$ is not necessarily the same as the configurational average of $|R_\alpha(t)|^2$, which characterizes the intensity of the fluorescence. We return to this point in Sec. V.

In the average t-matrix approach we calculate the matrix element of the t operator associated with a single trap, which we denote by $\langle\alpha|t_\mu(E)|\beta\rangle$. The configurational average of the diagonal matrix element of $G(E)$ is then given by

$$\langle\langle\alpha|G(E)|\alpha\rangle\rangle_c=[E-\epsilon_\alpha-N_T\langle\langle\alpha|t_\mu(E)|\alpha\rangle\rangle_c]^{-1}\,. \quad (2.2)$$

The t operator obeys the equation

$$t_\mu(E)=h_\mu+h_\mu g(E)t_\mu(E)\,, \qquad (2.3)$$

where h_μ denotes the interaction with the μth trap, Eq. (1.7), and $g(E)=(E-\mathcal{H}_0)^{-1}$, where $\mathcal{H}_0=\mathcal{H}-\mathcal{H}_I$ is the unperturbed Hamiltonian. Rather than working directly with the exciton states it is convenient to carry out the analysis in the site representation $|j\rangle$. The state $|j\rangle$ is related to the eigenstates through equations analogous to (1.3b) and (1.3d):

$$|\alpha\rangle=\sum_j X^*_{\alpha j}|j\rangle\,, \qquad (2.4a)$$

$$|j\rangle=\sum_\alpha X_{\alpha j}|\alpha\rangle\,, \qquad (2.4b)$$

so that

$$\langle\alpha|t|\beta\rangle=\sum_{i,j}\langle i|t|j\rangle X_{\alpha i}X^*_{\beta j}\,. \qquad (2.4c)$$

Using the site representation the t-matrix equation assumes the form

$$\langle i|t_\mu(E)|j\rangle=\sum_q\langle i|h_\mu|\mu;q\rangle\langle q;\mu|g(E)|\mu;q\rangle\langle\mu;q|h_\mu|j\rangle$$
$$+\sum_{l,m}\sum_{q,q'}\langle i|h_\mu|\mu;q\rangle\langle q;\mu|g(E)|\mu;q\rangle\langle q;\mu|h_\mu|l\rangle\langle l|g(E)|m\rangle\langle m|h_\mu|\mu;q'\rangle$$
$$\times\langle q';\mu|g(E)|\mu;q'\rangle\langle q';\mu|h_\mu|j\rangle+\cdots\,. \qquad (2.5)$$

A term-by-term examination shows that (2.5) is equivalent to the equation

$$\langle i|t_\mu(E)|j\rangle=v^\mu_{ij}(E)+\sum_{l,m}v^\mu_{il}(E)\langle l|g(E)|m\rangle\langle m|t_\mu(E)|j\rangle\,, \qquad (2.6)$$

where i, j, l, and m refer to donor sites in the vicinity of the trap μ. The symbol $v^\mu_{ij}(E)$ denotes an energy-dependent, nonlocal effective interaction which takes the form

$$v^\mu_{ij}(E)=\sum_q\langle i|h_\mu|\mu;q\rangle\langle q;\mu|g(E)|\mu;q\rangle\langle q;\mu|h_\mu|j\rangle$$
$$=\sum_q A^*_{\mu i}(q)(E-\omega_q-W_\mu)^{-1}A_{\mu j}(q)\,. \qquad (2.7)$$

Equations (2.1), (2.2), (2.4c), (2.6), and (2.7) constitute the formal solution to the problem to lowest order in N_T/N. At this point there are several comments which are appropriate. First, from (2.1) it is evident that we are interested in the behavior of $v^\mu_{ij}(E)$ for $E\approx\epsilon_\alpha$. This being the case we can write

$$v^\mu_{ij}(\epsilon_\alpha+i\epsilon)\approx\delta^\mu_{ij}-i\gamma^\mu_{ij}\,, \qquad (2.8)$$

where

$$\gamma^\mu_{ij}=\pi\sum_q A^*_{\mu i}(q)\delta(\epsilon_\alpha-\omega_q-W_\mu)A_{\mu j}(q) \qquad (2.9)$$

and

$$\delta^\mu_{ij}=\mathcal{P}\sum_q A^*_{\mu i}(q)(\epsilon_\alpha-\omega_q-W_\mu)A_{\mu j}(q)\,. \qquad (2.10)$$

Here we have made use of the symbolic identity $(x+i\epsilon)^{-1}=\mathcal{P}(1/x)-i\pi\delta(x)$, where $\mathcal{P}$ denotes the principal value. In most cases γ and δ will show only a weak dependence on exciton energy and trap depth, which we shall ignore. Second, if we keep only the first term on the right-hand side of (2.6) we obtain the Born approximation to the t matrix $\langle i|t_\mu(E)|j\rangle=v^\mu_{ij}(E)$. Finally, if each trap interacts with a single donor the t-matrix equation is readily solved with the result

$$\langle i|t_\mu(E)|j\rangle=\frac{\delta_{ij}(\delta^\mu_{jj}-i\gamma^\mu_{jj})}{1-(\delta^\mu_{jj}-i\gamma^\mu_{jj})\langle j|g(E)|j\rangle}\,. \qquad (2.11)$$

If $\delta^\mu_{jj}-i\gamma^\mu_{jj}$ is the same for all μ-j pairs the configurational average assumes a particularly simple form since we can equally well average over all j. In this case we have

$$\langle\langle\alpha|t(E)|\alpha\rangle\rangle_c=\frac{1}{N}\sum_j|X_{\alpha j}|^2\frac{(\delta-i\gamma)}{1-(\delta-i\gamma)\langle j|g(E)|j\rangle}\,. \qquad (2.12)$$

Note that if $\langle j|g(E)|j\rangle$ is independent of j we have the general result

$$\langle\langle \alpha | t(E) | \beta \rangle\rangle_c = \frac{\delta_{\alpha\beta}}{N} \frac{(\delta - i\gamma)}{[1 - (\delta - i\gamma)\langle j | g(E) | j \rangle]} , \tag{2.13}$$

the last equation following from (1.4a).

III. SYSTEMS WITH TRANSLATIONAL SYMMETRY

In this section we investigate the behavior of the probability amplitude in donor arrays with translational symmetry. In this situation the exciton modes are labeled by the wave vector $\vec{k}$ associated with the Brillouin zone of the donor lattice. Likewise the expansion coefficients $X_{\alpha j}$ take the form $N^{-1/2}\exp(i\vec{k}\cdot\vec{r}_j)$ where $\vec{r}_j$ denotes the position of the jth donor.

We first focus attention on a system where each acceptor is coupled to a single donor, which serves as a crude model for interstitial traps. Since all sites are equivalent, Eq. (2.12) reduces to

$$\langle\langle \vec{k} | t(E) | \vec{k} \rangle\rangle_c = \frac{\delta - i\gamma}{1 - (\delta - i\gamma) g_0(E)} , \tag{3.1}$$

where

$$g_0(E) = \frac{1}{N} \sum_{\vec{k}} (E - \epsilon_{\vec{k}})^{-1} , \tag{3.2}$$

$\epsilon_{\vec{k}}$ denoting the exciton energy $\epsilon_0 + \sum_j W_{ij} \times \{\exp[i\vec{k}\cdot(\vec{r}_0 - \vec{r}_j)] - 1\}$, with ϵ_0 the energy at the center of the zone. From (2.1) it follows that the probability amplitude is given by

$$\langle R_{\vec{k}}(t)\rangle_c = (i/2\pi) \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} \{\omega - \epsilon_{\vec{k}} - (N_T/N)(\delta - i\gamma) \times [1 - (\delta - i\gamma) g_0(\omega + i\epsilon)]^{-1}\}^{-1} . \tag{3.3}$$

The evaluation of this integral is discussed in the Appendix. The essential point is the behavior of the principal-value sum

$$B(\epsilon_{\vec{k}}) = \frac{1}{N} \mathcal{P} \sum_{\vec{k}'} (\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})^{-1} . \tag{3.4}$$

If $B(\epsilon_{\vec{k}})$ is finite then we can make use of (A7) with $A_\alpha \sim 8/N \ll N_T/N$. We find

$$\langle R_{\vec{k}}(t)\rangle_c = \exp\{-i\epsilon_{\vec{k}} t - it(N_T/N)(\delta - i\gamma) \times [1 - (\delta - i\gamma)B(\epsilon_{\vec{k}})]^{-1}\} , \tag{3.5}$$

from which it follows that the amplitude decays exponentially at the rate

$$\Gamma_{\vec{k}} = \frac{(N_T/N)\gamma}{[1 - \delta B(\epsilon_{\vec{k}})]^2 + [\gamma B(\epsilon_{\vec{k}})]^2} . \tag{3.6}$$

The numerator in (3.6) is the "golden-rule" decay rate.[5] The denominator is a correction to the Born approximation. If $\delta \ll \gamma$, as is often the case, then the correction amounts to a reduction by the factor $1 + [\gamma B(\epsilon_{\vec{k}})]^2$. This factor arises from the interplay between phonon-assisted transfer to the traps and coherent transfer among the donors. Loosely speaking, we have $B(\epsilon_{\vec{k}}) \approx \Delta E^{-1}$ where ΔE is the exciton bandwidth. Thus when the exciton band is broad, $\Delta E \gg \gamma$, we have $\Gamma \approx (N_T/N)\gamma$, whereas in the narrow band limit we obtain a much slower decay $\Gamma \approx (N_T/N)(\Delta E)^2\gamma^{-1}$. These results have a simple physical interpretation. When the band is broad, excitation is rapidly transferred throughout the array and thus can quickly reach a trap. When the band is narrow, the excitation moves slowly so that it takes a long time for it to be trapped.

As noted in the Appendix the principal value sum (3.4) diverges for the $\vec{k} = 0$ mode in one and two dimensions. From Eq. (A11) we infer the nonexponential asymptotic behavior

$$\langle R_0(t)\rangle_c \sim \frac{L}{N_T} \frac{e^{-i\epsilon_0 t}}{(4\pi D t)^{1/2}} , \quad t \to \infty \tag{3.7}$$

in one dimension and

$$\langle R_0(t)\rangle_c \sim \frac{A}{N_T} \frac{e^{-i\epsilon_0 t}}{(4\pi D t)} , \quad t \to \infty \tag{3.8}$$

in two dimensions. Here L and A denote the length and area of the array, respectively, while D is the coefficient of the k^2 term in the expansion of $\epsilon_{\vec{k}}$ about $\vec{k} = 0$. The nonexponential decay of $\langle R_0(t)\rangle_c$ in one and two dimensions is reminiscent of the nonexponential decay of the integrated donor fluorescence in the incoherent transfer problem.[6]

As a second example we consider the decay of the $\vec{k} = 0$ mode in a system where the traps are substitutional impurities. Assuming nearest-neighbor interactions between donors and acceptors, transfer to the trap can take place from any one of the z equivalent nearest-neighbor sites. The t-matrix equation has the form shown in Eq. (2.6) with i and j denoting nearest neighbors of the impurity. In the case of the $\vec{k} = 0$ mode the configurational average takes the form

$$\langle\langle 0 | t | 0 \rangle\rangle_c = \frac{1}{N} \sum_{i,j} \langle i | t | j \rangle , \tag{3.9}$$

since the result obtained by summing over nearest neighbors is independent of the location of the trap.

The t-matrix equation is readily solved for the partial sum

$$T_i = \sum_j \langle i | t | j \rangle . \tag{3.10}$$

We obtain

$$T_i = \sum_j v_{ij} + \sum_{l,m} v_{il} \langle l | g | m \rangle T_m . \quad (3.11)$$

Since all nearest-neighbor sites are equivalent, T_i is independent of i. Thus we have

$$\langle\langle 0 | t(E) | 0 \rangle\rangle_c = z T_i / N$$
$$= \frac{z}{N} \frac{\sum_j (\delta_{ij} - i\gamma_{ij})}{1 - \sum_{j,l} (\delta_{ij} - i\gamma_{ij}) \langle j | g(E) | l \rangle} , \quad (3.12)$$

where γ_{ij} and δ_{ij} are given by (2.9) and (2.10), respectively, and

$$\langle j | g(E) | l \rangle = \frac{1}{N} \sum_{\vec{k}} \frac{\exp[i\vec{k} \cdot (\vec{r}_j - \vec{r}_l)]}{E - \epsilon_{\vec{k}}} , \quad (3.13)$$

j and l referring to nearest neighbors of the trap. From Eqs. (3.12) and (3.13) we conclude that in three dimensions $\langle R_0(t) \rangle_c$ decays exponentially at the rate

$$\Gamma_0 = \frac{N_T}{N} \operatorname{Re} \left(\frac{z \sum_j (\delta_{ij} - i\gamma_{ij})}{1 - \sum_{j,l} (\delta_{ij} - i\gamma_{ij}) \langle j | g(\epsilon_0) | l \rangle} \right) , \quad (3.14)$$

where Re denotes real part.

Finally, it should be noted that the asymptotic behavior of $\langle R_0(t) \rangle_c$ in one and two dimensions, which is displayed in Eqs. (3.7) and (3.8), is valid for interactions of arbitrary range. This is a consequence of the fact that in the limit $E \to \epsilon_0$ the sum in (3.13) is dominated by the terms with $\vec{k} \approx 0$. When this happens the matrix elements $\langle j | g(E) | l \rangle$ diverge, becoming independent of $\vec{r}_j - \vec{r}_l$. As long as $\langle j | g(E) | l \rangle$ is independent of j and l the t-matrix equation can be solved for the sum $\sum_{i,j} \langle i | t | j \rangle$. Equations (3.7) and (3.8) then follow from an analysis similar to that shown in Eqs. (A8)–(A11).

IV. DISORDERED SYSTEMS

The analysis of the trapping in systems where the array of donors is itself disordered is complicated, depending in detail on the eigenfunctions and eigenvalues of $\mathcal{H}_D$. We will consider only the case where each trap interacts with a single donor, which is an appropriate approximation when the donor array is itself dilute. In this case the configurational average of $\langle \alpha | t | \alpha \rangle$ takes the form [cf. (2.11)]

$$\langle\langle \alpha | t(E) | \alpha \rangle\rangle_c = \frac{-i}{N} \sum_j |X_{\alpha j}|^2 \int \frac{Y(\gamma)\gamma d\gamma}{1 + i\gamma \langle j | g(E) | j \rangle} , \quad (4.1)$$

assuming δ^{μ}_{jj} can be set equal to zero. In writing (4.1) we have allowed for a distribution in γ arising from the variation in donor-acceptor separation. Thus $Y(\gamma) d\gamma$ is the probability that the transfer rate lies between γ and $\gamma + d\gamma$.

The behavior of $\langle\langle \alpha | t | \alpha \rangle\rangle_c$ is influenced by $\langle j | g(E) | j \rangle$. Expanded in terms of eigenstates this function takes the form

$$\langle j | g(E) | j \rangle = \sum_\beta |X_{j\beta}|^2 (E - \epsilon_\beta)^{-1} . \quad (4.2)$$

Insight into the meaning of this function can be obtained by writing it as an integral:

$$\langle j | g(E) | j \rangle = \frac{1}{N} \int dE' \rho_j(E') (E - E')^{-1} , \quad (4.3)$$

where

$$\rho_j(E) = N \sum_\beta |X_{j\beta}|^2 \delta(E - \epsilon_\beta) \quad (4.4)$$

is the local density of states associated with the jth donor.

At this point it is convenient to consider two limiting situations. The first pertains to systems where the exciton modes are delocalized, that is to say $|X_{j\alpha}|^2 \approx 1/N$ for all donors. When this happens we expect the local density of states to be nearly the same for all j. Under these circumstances it is a reasonable approximation to replace the local density of states by its global average $\rho(E)$:

$$\rho_j(E) \to \frac{1}{N} \sum_j \rho_j(E) = \sum_\beta \delta(E - \epsilon_\beta) = \rho(E) , \quad (4.5)$$

having made use of (1.4a).

Using (1.4a) a second time we obtain the result

$$\langle\langle \alpha | t(E) | \alpha \rangle\rangle_c = \frac{-i}{N} \int \frac{Y(\gamma)\gamma d\gamma}{1 + (i\gamma/N) \int \rho(E')(E - E')^{-1} dE'} . \quad (4.6)$$

From (4.6) and (A7) we conclude that $\langle R_\alpha(t) \rangle_c$ decays exponentially at a rate Γ_α given by

$$\Gamma_\alpha = \frac{N_T}{N} \int Y(\gamma)\gamma \, d\gamma \left[1 + \left(\gamma \frac{1}{N} \mathcal{P} \int \frac{\rho(E') dE'}{\epsilon_\alpha - E'} \right)^2 \right]^{-1} , \quad (4.7)$$

provided the principal-value integral is finite.

The other case corresponds to the opposite limit where the mode α is confined entirely to the $\bar{j}$th donor, i.e., $X_{\alpha j} = \delta_{j\bar{j}}$. When this happens we have

$$\langle\langle \alpha | t(E) | \alpha \rangle\rangle_c = \frac{-i\gamma_{\bar{j}\bar{j}}/N}{1 + i\gamma_{\bar{j}\bar{j}}/(E - \epsilon_\alpha)} . \quad (4.8)$$

From Eq. (A7) of the Appendix we obtain the result

$$\langle R_\alpha(t) \rangle_c = \frac{e^{-i\epsilon_\alpha t}}{1 + N_T/N} + \frac{N_T/N e^{-i\epsilon_\alpha t}}{1 + N_T/N} \exp[-\gamma_{\bar{j}\bar{j}}(1 + N_T/N)t] , \quad (4.9)$$

which reduces to

$$\langle R_\alpha(t)\rangle_c = (1 - N_T/N)e^{-i\epsilon_\alpha t} + (N_T/N)e^{-i\epsilon_\alpha t}\exp(-\gamma_{\bar{j}\bar{j}}t)\,, \tag{4.10}$$

in light of the assumption $N_T/N \ll 1$. Equation (4.10) has a simple physical interpretation: $1 - N_T/N$ is the probability that there is no trap associated with the $\bar{j}$th donor, N_T/N is the probability that a trap is present. When this is the case the amplitude decays at the rate $\gamma_{\bar{j}\bar{j}}$.

The decay of a mode which is intermediate between those limits is more complicated. In order to gain insight into the problem we consider a simple model where the mode is confined to N_L donors ($1 \leq N_L \leq N$). We assume that $|X_{\alpha j}|^2 = 1/N_L$ if j is one of the N_L donors and zero otherwise. For donors in this set the local density of states is approximated by

$$\rho_j(E) = (N/N_L)\delta(E - \epsilon_\alpha) + (1 - N_L^{-1})\rho(E)\,, \tag{4.11}$$

which interpolates between the two limits mentioned above. This approximation satisfies the sum rule

$$\int \rho_j(E)dE = N\,, \tag{4.12}$$

following from (1.4b).

Taking γ to be the same for all sites we obtain the result

$$\langle\langle \alpha | t(E) | \alpha\rangle\rangle_c = -i\gamma N^{-1}\left(1 + i\gamma N_L^{-1}(E - \epsilon_\alpha)^{-1} + i\gamma(1 - N_L^{-1})N^{-1}\mathcal{P}\int \frac{\rho(E')}{E - E'}dE'\right)^{-1}. \tag{4.13}$$

Equation (4.13) together with (A7) leads to

$$\langle R_\alpha(t)\rangle_c = \frac{e^{-i\epsilon_\alpha t}}{1+C} + \frac{Ce^{-i\epsilon_\alpha t}}{1+C}\exp\left[-(\gamma/N_L)t(1+C)\left(1 + i\gamma(1 - N_L^{-1})N^{-1}\mathcal{P}\int\frac{\rho(E')dE'}{\epsilon_\alpha - E'}\right)^{-1}\right], \tag{4.14}$$

where $C = (N_T/N)N_L$ is the mean number of traps associated with the N_L donors participating in the mode. An interesting aspect of (4.14) is that when $C \gg 1$, which necessitates $N_L \gg 1$ since $N_T/N \ll 1$ by assumption, the decay of the localized mode is indistinguishable from that of a macroscopically delocalized mode where $N_L \simeq N$.

In the opposite limit, $C \ll 1$, Eq. (4.14) takes the form

$$\langle R_\alpha(t)\rangle_c = (1 - C)e^{-i\epsilon_\alpha t} + Ce^{-i\epsilon_\alpha t}\exp\left[-(\gamma/N_L)t\left(1 + i\gamma(1 - N_L^{-1})N^{-1}\mathcal{P}\int\frac{\rho(E')dE'}{(\epsilon_\alpha - E')}\right)^{-1}\right], \tag{4.15}$$

analogous to (4.10). Equation (4.15) has a simple physical interpretation. Assuming the traps have a Poisson distribution with mean C, then to order C the quantity $(1 - C)$ is the probability that there are no traps associated with the state α, while to the same order C is the probability of there being a single trap associated with one of the N_L sites. Probabilities of configurations with more than one trap are of order C^2 and higher and hence can be neglected when $C \ll 1$. The second term in (4.15) described the decay in the presence of a single trap; the first term characterizes the behavior when no traps are present. In this situation when there are also interactions which transfer excitation between exciton modes, trapping can take place in a two-step process involving incoherent transfer to a state having one or more traps.

V. SUMMARY AND DISCUSSION

In this paper we have outlined a calculation of the configurational average of the probability amplitude characterizing the decay of an exciton in a system with a random distribution of traps. The results apply to situations where the number of traps is much less than the number of donor ions. The distinction is made between donor arrays with translational symmetry and those which are disordered. In ordered arrays in three dimensions the probability amplitude decays exponentially. The rate of decay depends on the range and strength of the donor-acceptor transfer. In a system where each trap is coupled to a single donor the rate is given by (3.6). When the trap is a substitutional impurity which interacts only with its nearest neighbors the rate of decay of the $\vec{k} = 0$ mode has the form shown in (3.14). As a by-product of our analysis we learn that the Born approximation to the decay rate is only valid when

$$\frac{\gamma}{N}\mathcal{P}\sum_{\vec{k}'}(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})^{-1} \ll 1\,. \tag{5.1}$$

In the case of one- and two-dimensional arrays we find that the asymptotic amplitude of the $\vec{k} = 0$ mode does not decay exponentially. Instead, in one dimension we obtain $\langle R_0(t)\rangle_c \sim t^{-1/2}$ [Eq. (3.7)] while in two dimensions we have $\langle R_0(t)\rangle_c \sim t^{-1}$ [Eq. (3.8)]. Both of these results are universal in the sense that (3.7) and (3.8) are independent of the strength and range of the donor-acceptor transfer.

With disordered arrays the distinction is made between localized and extended modes. When the modes are delocalized the approximate decay rate is given by (4.7) (provided the principal-value integral is finite). In the extreme case where the mode is localized on a single donor, $\langle R_\alpha(t)\rangle_c$ is given by (4.10). In the intermediate situation where the mode is associated with N_L donors the amplitude is crudely approximated by (4.14).

We next address the question of the relation of our results to various experimental studies. The essential point here is that what we have calculated is the probability amplitude averaged over trap configurations. What is measured in laboratory studies of fluorescence decay is $|\hat{R}_\alpha(t)|^2$, where $\hat{R}_\alpha(t)$ is the amplitude associated with the configuration of traps appropriate to the sample under investigation. From Eqs. (4.9) and (4.14) it is evident that when the mode α is strongly localized, $|\langle R_\alpha(t)\rangle_c|^2$ cannot be equated with $|\hat{R}_\alpha(t)|^2$. On physical grounds we can conclude that the approximations leading to (4.14) are equivalent to

$$\langle |R_\alpha(t)|^2\rangle_c = \frac{1}{1+C} + \frac{Ce^{-2\Gamma_\alpha t}}{1+C} , \tag{5.2}$$

with

$$\Gamma_\alpha = (\gamma/N_L)(1+C)\left[1+\left(\gamma(1-N_L^{-1})N^{-1})\mathcal{P}\int\frac{dE'\rho(E')}{\epsilon_\alpha - E'}\right)^2\right]^{-1}. \tag{5.3}$$

Likewise on physical grounds we argue that when the mode α is delocalized in the sense that there is significant amplitude on a macroscopic number of occupied donor sites we have

$$|\langle R_\alpha(t)\rangle_c|^2 \approx |\hat{R}_\alpha(t)|^2 . \tag{5.4}$$

The reasoning is as follows. Since the donor-acceptor transfer rates fall off rapidly with distance (r^{-6} for dipole-dipole transfer) the decay of the exciton wave function at the point $\vec{r}_j$ is primarily sensitive to the configuration of traps in the vicinity of $\vec{r}_j$. Thus a wave function extending over many donors samples many local trap configurations. When this happens the wave function associated with a single global trap configuration gives rise to a time-dependent fluorescent intensity which is experimentally indistinguishable from that proportional to $|\langle R_\alpha(t)\rangle_c|^2$.

Recently, experiments have been carried out in ruby[7] which have been interpreted as providing evidence of a mobility edge between localized and extended states.[8] It is beyond the scope of this paper to discuss these experiments in detail. However, from Eqs. (14.14) and (5.2), it is evident that when $C \gg 1$ the decay from a localized donor state is indistinguishable from that of a macroscopically extended state ($N_L \approx N$). Taking $C=1$, i.e., an average of one trap per N_L sites as a criterion, we conclude that fluorescence experiments can only distinguish between states with $N_L \ll N/N_T$ and $N_L \gg N/N_T$. Since the samples studied in Ref. 7 have $N/N_T \approx 400$ (for a Cr^{3+} concentration $c \approx 0.16\%$ and a trap concentration $\frac{3}{2}c^2$) it is impossible in principle to determine if the states involve more than 10^2–10^3 donors. However, in this case the distinction between $N_L = 10^3$ and $N_L = 10^{23}$ is probably not important for determining the location of a mobility edge.

Finally, we would like to emphasize the difference between systems where incoherent donor-donor transfer is dominant and those where the transfer takes place coherently. Since the incoherent transfer rates fall rapidly with decreasing temperature by going to very low temperatures it may be possible to see a crossover from incoherent to coherent behavior. Systematic studies of the fluorescence decay in both regimes which were carried out on the same sample would be particularly worthwhile. Measurements of the decay in quasi-one- and two-dimensional materials could be extremely interesting in that they hold the promise of testing the behavior predicted by (3.7) and (3.8) as well as the corresponding results for incoherent transfer.[6]

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APPENDIX

In this Appendix we discuss the evaluation of the integral for $\langle R_\alpha(t)\rangle_c$ which is defined by

$$\langle R_\alpha(t)\rangle_c = \left(\frac{i}{2\pi}\right)\int_{-\infty}^{\infty} d\omega\,[\omega + i\epsilon - \epsilon_\alpha - f(\omega + i\epsilon)]^{-1} , \tag{A1}$$

where

$$f(E) = \frac{-i\gamma(N_T/N)}{1+i\gamma\sum_\beta |X_{j\beta}|^2/(E-\epsilon_\beta)} \tag{A2}$$

and $\epsilon \to 0+$. At long times the dominant contribution to the integral comes from $\bar{\omega} = \omega - \epsilon_\alpha \approx 0$. As a result, in (A2) we must single out the terms where $\epsilon_\beta = \epsilon_\alpha$. Thus we have

$$f(E) = \frac{-i\gamma(N_T/N)}{1+i\gamma A_\alpha/(E-\epsilon_\alpha) + i\gamma B_\alpha(E)} , \tag{A3}$$

in which

$$A_\alpha = \sum_{\beta, E_\beta = E_\alpha} |X_{j\beta}|^2 \tag{A4}$$

and

$$B_\alpha(E)=\sum_{\beta, E_\beta\neq E_\alpha}|X_{j\beta}|^2(E-\epsilon_\beta)^{-1}. \tag{A5}$$

From (A5) it is evident that $B_\alpha(\epsilon_\alpha)$ can be written

$$B_\alpha(\epsilon_\alpha)=\mathcal{P}\sum_\beta |X_{j\beta}|^2(\epsilon_\alpha-\epsilon_\beta)^{-1}, \tag{A6}$$

where $\mathcal{P}$ denotes the principal value. Provided the principal value is finite we can evaluate the integral with $B_\alpha(\epsilon_\alpha)$ in place of $B_\alpha(\omega+i\epsilon)$. Closing the contour in the lower half-plane we obtain as a result

$$\langle R_\alpha(t)\rangle_c=e^{-i\epsilon_\alpha t}\left(\frac{A_\alpha}{A_\alpha+(N_T/N)}+\frac{(N_T/N)}{A_\alpha+(N_T/N)}\exp\{-\gamma t[A_\alpha+(N_T/N)][1+i\gamma B_\alpha(\epsilon_\alpha)]^{-1}\}\right). \tag{A7}$$

In one and two dimensions the principal-value integral diverges for the $\vec{k}=0$ mode. Writing $\epsilon_{\vec{k}}-\epsilon_0=Dk^2$ we have for one dimension,

$$\frac{1}{N}\sum_k\frac{1}{(\epsilon_0+\Delta E-\epsilon_k)}\sim\int\frac{dk}{\Delta E-Dk^2}\sim|\Delta E|^{-1/2} \tag{A8}$$

and for two dimensions,

$$\frac{1}{N}\sum_{\vec{k}}\frac{1}{(\epsilon_0+\Delta E-\epsilon_{\vec{k}})}\sim\ln|\Delta E| \tag{A9}$$

as $|\Delta E|\to 0$. Thus in the limit $|\Delta E|\to 0$ we obtain

$$f(\epsilon_0+\Delta E)\sim-\frac{N_T}{N}\left(\frac{1}{N}\sum_{\vec{k}}\frac{1}{\Delta E-Dk^2}\right)^{-1}. \tag{A10}$$

In light of the behavior shown in Eqs. (A8) and (A9) it is evident that $f(\epsilon_0+\Delta E)$ dominates the denominator in (A1). Hence in the long-time limit, which corresponds to $\Delta E\to 0$, we have

$$\langle R_0(t)\rangle_c=e^{-i\epsilon_0 t}\frac{1}{N_T}\sum_{\vec{k}}e^{-iDk^2t}. \tag{A11}$$

Converting the sum to an integral ($-\infty\leq k\leq\infty$) in one and two dimensions we obtain (3.7) and (3.8), respectively.

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