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Donor fluorescence at high trap concentration

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We investigate the time development of the donor fluorescence in the presence of a high concentration of acceptor ions which act as traps for the excitation. It is assumed that the transfer rates between donors are symmetric and independent of the energy mismatch and that there is no back transfer from the traps. The donor and acceptor ions are randomly distributed on a lattice with site occupation probabilities c_D and c_A, respectively. We specialize to the case of dipole-dipole transfer between donors and from donors to acceptors. For a dilute system, c_D, $c_A \ll 1$, we use a coherent-potential approximation to calculate the Laplace transform of the donor fluorescence-decay curve for all values of the ratio c_A/c_D. It is argued that the theory should apply when the microscopic transfer rate between donor ions is at least as large as the corresponding transfer rate from donors to acceptors.

I. INTRODUCTION

In a recent paper,[1] hereafter referred to as I, we presented a general theory for the time development of the donor fluorescence in the presence of a random distribution of acceptor ions which act as traps for the excitation. The theory was based on a set of coupled rate equations for the donor array. It was assumed that the donor-donor transfer rates were symmetric and independent of the energy mismatch between ions and that there was no back transfer from the traps. Exact results were obtained in the static and rapid-transfer limits. A theory based on the average t matrix approximation was developed for the regime intermediate between the two limits, which is applicable whenever the concentration of acceptors is much less than the donor concentration.

In this paper we extend the analysis of I to systems having a relatively high concentration of acceptor ions. The theory applies to cases where both the donor and acceptor arrays are dilute. There is a lattice of sites that is occupied at random by donors or acceptors, with probabilities c_D and c_A, respectively, where both $c_A, c_D \ll 1$. However, unlike I, we do not necessarily assume $c_A \ll c_D$. We consider in detail only the case where both the donor-donor and donor-acceptor transfer are governed by a dipolar mechanism and hence fall off as the inverse sixth power of the separation between the ions. Writing the donor-acceptor transfer rate as α/r^6 and the donor-donor rate as β/r^6 we further restrict the analysis to systems in which $\alpha \lesssim \beta$, i.e., where the donor-donor transfer is at least as rapid as the donor-acceptor transfer.

We follow the notation of I and write the normalized intensity of the donor fluorescence $F(t)$ as

$$F(t) = e^{-\gamma_R t} f(t) , \tag{1.1}$$

where γ_R^{-1} is the radiative lifetime. The function $f(t)$ characterizes the loss due to one-way transfer to traps. In I it was shown that when $c_A \ll c_D$ the Laplace transform of $f(t)$, defined by

$$\hat{f}(s) = \int_0^\infty dt\, e^{-st} f(t) , \tag{1.2}$$

could be written in the average t matrix approximation in the form

$$\hat{f}(s) = \left(s + c_A \sum_{l,l'} t_{ll'}(s) \right)^{-1} , \tag{1.3}$$

where the t matrix is obtained as the solution to the equation

$$t_{ll'} = X_{0l} \delta_{ll'} - \sum_{l''} X_{0l} \langle g_{ll''}(s) \rangle_c t_{l''l'}(s) , \tag{1.4}$$

in which X_{0l} is the transfer rate from a donor at site l to an acceptor at site o. The symbol $\langle g_{ll'}(t) \rangle_c$ denotes the configurational average of a Green's function characterizing the transfer of excitation in the absence of traps.

It was argued in I that when the donor-donor transfer is rapid in comparison with the donor-acceptor transfer it is a reasonable approximation to neglect the off-diagonal elements of the t matrix. When this is done the solution to Eq. (1.4) takes the form

$$t_{ll} = X_{0l} / [1 + X_{0l} \hat{R}_0(s)] , \tag{1.5}$$

where $\hat{R}_0(s) = \langle g_{ll}(s) \rangle_c$. In this case $\hat{f}(s)$ becomes

$$\hat{f}(s) = \left(s + c_A \sum_l X_{0l} / [1 + X_{0l} \hat{R}_0(s)] \right)^{-1} , \tag{1.6}$$

in which the sum on l is over sites in the neighborhood of site o.

Passing to the continuum limit we can approximate the sum in Eq. (1.6) by an integral, viz.,

$$c_A \sum_l \frac{X_{0l}}{1+X_{0l}\hat{R}_0(s)} \rightarrow n_A \int \frac{d\vec{r}\, x(r)}{1+x(r)\hat{R}_0(s)} , \qquad (1.7)$$

where n_A is the number of acceptors per unit volume. For the case of dipole-dipole transfer $x(r) = \alpha/r^6$, the integral is written

$$4\pi\alpha \int_{r_c}^{\infty} \frac{r^2 dr}{r^6 + \alpha \hat{R}_0(s)} ,$$

where r_c is the minimum donor-acceptor separation. Provided $(\alpha/r_c^6)\hat{R}_0(s) \gg 1$, which will be the case for c_D sufficiently small, we can take the lower limit to be zero thus obtaining the result $(\frac{2}{3}\pi^2)[\alpha/\hat{R}_0(s)]^{1/2}$ so that we have[2]

$$\hat{f}(s) = \{s + (\tfrac{2}{3}\pi^2) n_A [\alpha/\hat{R}_0(s)]^{1/2}\}^{-1} . \qquad (1.8)$$

In I, $\hat{R}_0(s)$ was identified as the Laplace transform of the configurational average of the conditional probability that a donor ion excited at $t=0$ is still excited at a later time t. Writing this average as $R_0(t)$ we obtain

$$\hat{R}_0(s) = \int_0^{\infty} e^{-st} R_0(t)\, dt , \qquad (1.9)$$

where the 0 signifies the value in the absence of donor-acceptor transfer. It was also pointed out for the case of dipole-dipole transfer between donors that when $c_D \ll 1$, a reasonable approximation is to take

$$R_0(t) = \exp[-(\Delta_{DD}/2^{1/2}) t^{1/2}] , \qquad (1.10)$$

in which

$$\Delta_{DD} = (\tfrac{4}{3}\pi^{3/2}) n_D \beta^{1/2} , \qquad (1.11)$$

n_D being the number of donors per unit volume. The accuracy of Eq. (1.10), which is essentially equivalent to the "pair approximation" of Lyo[3] and the "three-body" approximation of Gochanour *et al.*,[4] has been verified out to times such that $R_0(t) \approx 0.05$ for $c_D = 0.01$.[5]

Using Eq. (1.10) we obtain the result

$$R_0(s) = s^{-1}\{1 - \sqrt{\pi}[\Delta_{DD}/(2^{3/2} s^{1/2})] \times \exp[\Delta_{DD}^2/(8s)]\, \mathrm{erfc}[\Delta_{DD}/(2^{3/2} s^{1/2})]\} , \qquad (1.12)$$

where erfc$[x]$ denotes the complementary error function.[6] Note that Eq. (1.12) has the limiting behavior

$$\hat{R}_0(s) \approx 4/\Delta_{DD}^2 , \qquad (1.13)$$

for $\Delta_{DD}/s \gg 1$, and

$$\hat{R}_0(s) \approx 1/s , \qquad (1.14)$$

for $\Delta_{DD}/s \ll 1$.

As long as $\alpha \lesssim \beta$ and $c_D \ll 1$, Eqs. (1.8) and (1.12) characterize the transform of $f(t)$ in the limit $c_A/c_D \ll 1$. In Sec. II we outline a generalization of these equations which is appropriate for all values of c_A/c_D.

II. COHERENT-POTENTIAL APPROXIMATION

The theory outlined in Sec. I is applicable only when $c_A/c_D \ll 1$. We can extend our results to arbitrary values of this ratio by using a variation of the coherent-potential approximation (CPA) which has been shown to be remarkably accurate in analogous calculations for disordered alloys and magnets.[7] As can be seen from the microscopic rate equations given in I the rate at which the nth donor transfers to neighboring traps X_n is a random variable when the traps are distributed at random even when the donor array has translational symmetry. Since we neglect transfer from the acceptors to the donors, the randomness associated with the donor-acceptor transfer is confined to the diagonal elements of the rate equations (site-diagonal disorder). Neglecting the off-diagonal elements of the t-matrix equation, which we have argued is a reasonable approximation when $\alpha \lesssim \beta$, is equivalent to assuming that there are no correlations between neighboring donors in the donor-acceptor transfer process. In the CPA, when this happens, we need consider only the dynamics of a single acceptor embedded in a background incorporating the effect of donor-donor and donor-acceptor transfer involving neighboring ions.

As long as there is only site-diagonal disorder (no back transfer from traps) the CPA appropriate to this situation leads to an expression for $\hat{f}(s)$ of the form[7]

$$\hat{f}(s) = [s + X_{CPA}(s)]^{-1} , \qquad (2.1)$$

where the s-dependent decay rate $X_{CPA}(s)$ satisfies the equation

$$\int_0^{\infty} \frac{dX\, \mathcal{P}(X)[X - X_{CPA}(s)]}{1 + [X - X_{CPA}(s)]\hat{R}(s)} = 0 . \qquad (2.2)$$

Here $\mathcal{P}(X)$ is the normalized probability distribution of the variable X_n. The function $\hat{R}(s)$ is the Laplace transform of the conditional probability $R(t)$ that a donor excited at $t=0$ is still excited at a later time t calculated in the presence of the traps, viz.,

$$\hat{R}(s) = \int_0^{\infty} dt\, e^{-st} R(t) . \qquad (2.3)$$

Since the donor array is itself dilute and random, we depart from the standard form for $R(t)$,[7] which is appropriate when the donors form a periodic array, and write it as a product

$$R(t) = f_0(t) R_0(t), \tag{2.4}$$

where $R_0(t)$ is $R(t)$ in the absence of donor-acceptor transfer [Eq. (1.10) in the case of dipole-dipole transfer]. The function $f_0(t)$ is $f(t)$ in the absence of donor-donor transfer and is given by an equation derived by Inokuti and Hirayama.[8] It is related to $\mathcal{P}(X)$ through the integral

$$f_0(t) = \int_0^\infty dX\, e^{-Xt} \mathcal{P}(X). \tag{2.5}$$

Equation (2.4) for $R(t)$ is obtained as the low-concentration limit, $c_D, c_A \ll 1$, of the more general expression

$$R(t) = \prod_l \left[1 - c_A - c_D + c_A e^{-X_{lo}t} + c_D e^{-W_{lo}t} \cosh(W_{lo}t)\right], \tag{2.6}$$

where X_{lo} is the transfer rate from a donor at site o to an acceptor at site l, and W_{lo} is the transfer rate from a donor at site o to a donor at site l. Equation (2.6) is the generalization of model 2 of Huber *et al.*[9] to include one-way transfer to traps as well as multiple exchanges of excitation between nearby donors and one-way transfer to distant donors. It reduces to Eq. (2.4) when the product is written as the exponential of a sum of logarithms, the latter are expanded to first order in c_A and c_D, and the corresponding sums are replaced by integrals.

Equations (2.1) and (2.5) constitute the coherent-potential approximation to the transform of the normalized decay curve. We will discuss numerical solutions appropriate to dipole-dipole transfer in Sec. III. First, however, we show that Eq. (2.1) reproduces known results in appropriate limits. When $c_A \to 0$, and c_D is fixed, we have $\hat{R}(s) = \hat{R}_0(s)$. In addition we can neglect X_{CPA} in the denominator of Eq. (2.2), thus obtaining the equation

$$\int_0^\infty \frac{dX\, X_{\text{CPA}}(s) \mathcal{P}(X)}{1 + X\hat{R}_0(s)} = \int_0^\infty \frac{dX\, X \mathcal{P}(X)}{1 + X\hat{R}_0(s)}. \tag{2.7}$$

Since in the limit $c_A \to 0$, $\mathcal{P}(X)$ has most of its weight near $X = 0$ [cf. Eq. (3.1)], we can neglect $X\hat{R}_0(s)$ in the denominator of the left-hand side of Eq. (2.7). As a result we have

$$X_{\text{CPA}}(s) = \int_0^\infty \frac{dS\, X \mathcal{P}(X)}{1 + X\hat{R}_0(s)}, \tag{2.8}$$

which leads to an equation equivalent to (1.6) to first order in c_A.

In the opposite limit, $c_D \to 0$ and c_A is fixed, or when there is negligible donor-donor transfer, we have $R_0(t) = 1$. In this case Eq. (2.2) takes the form

$$\int_0^\infty \frac{dX [X - X_{\text{CPA}}(s)] \mathcal{P}(x)}{1 + [X - X_{\text{CPA}}(s)] \hat{f}_0(s)} = 0, \tag{2.9}$$

where $\hat{f}_0(s)$ is the transform of $f_0(t)$. Equation (2.9) has the solution

$$X_{\text{CPA}}(s) = \hat{f}_0(s)^{-1} - s. \tag{2.10}$$

To verify this we insert Eq. (2.10) into the denominator of Eq. (2.9), obtaining as a result

$$\int_0^\infty \frac{dX\, \mathcal{P}(X)(X - X_{\text{CPA}})}{1 + (X - \hat{f}_0^{-1} + s)\hat{f}_0} = \hat{f}_0^{-1} - \hat{f}_0^{-1}(X_{\text{CPA}} + s) \int_0^\infty \frac{\mathcal{P}(X)\, dX}{X + s} = 0. \tag{2.11}$$

Solving for X_{CPA} we have

$$X_{\text{CPA}}(s) = \left[\int_0^\infty dX \mathcal{P}(X)(X + s)^{-1}\right]^{-1} - s, \tag{2.12}$$

which reduces to Eq. (2.10) in light of Eq. (2.5). Inserting Eq. (2.10) into Eq. (2.1), we find

$$\hat{f}(s) = \hat{f}_0(s), \tag{2.13}$$

as expected.

The final example corresponds to the case of (infinitely) rapid donor-donor transfer.[1] In this case we can neglect the term $(X - X_{\text{CPA}})\hat{R}(s)$ in the denominator of Eq. (2.2) obtaining as a result

$$X_{\text{CPA}} = \int_0^\infty dX\, X \mathcal{P}(X), \tag{2.14}$$

independent of s. Using Eq. (2.14) we find

$$f(t) = \exp\left[-t \int_0^\infty dX X \mathcal{P}(X)\right] = \exp\left(-c_A \sum_l W_{ol}\, t\right), \tag{2.15}$$

in agreement with the results of I.

III. DIPOLE-DIPOLE TRANSFER

Here we apply the general theory developed in Sec. II to the special case where both the donor-donor transfer and the donor-acceptor transfer are governed by dipolar processes. With the donor-acceptor rate varying as α/r^6 and the donor-donor rate as β/r^6, we have for the probability distribution $\mathcal{P}(X)$ introduced in the Sec. II,[10]

$$\mathcal{P}(X) = (\Delta_{\text{DA}}^2/4\pi X^3)^{1/2} \exp[-(\Delta_{\text{DA}}^2/(4X)], \tag{3.1}$$

where

$$\Delta_{\text{DA}} = (\tfrac{4}{3}\pi^{3/2}) n_A \alpha^{1/2}, \tag{3.2}$$

n_A being the concentration of acceptors. It should be noted that Eq. (3.1) is the normalized distribution for the interval $0 \leqslant X \leqslant \infty$. Strictly speaking, one should use a distribution which is restricted to a finite interval with an upper limit corresponding to the transfer rate at minimum donor-acceptor separation r_c. However as long as $(\alpha/r_c^6)\hat{R}(s) \gg 1$ our results are essentially the same as obtained with $r_c = 0$.

Using Eqs. (3.1) and (3.2) in Eq. (2.5) we find

$$f_0(t) = \exp(-\Delta_{DA} t^{1/2}), \tag{3.3}$$

which when combined with Eqs. (1.10), (2.3), and (2.4) leads to the result

$$\hat{R}(s) = s^{-1}\{1 - \sqrt{\pi}[\Delta_T/(2s^{1/2})] \times \exp[\Delta_T^2/(4s)]\,\mathrm{erfc}[\Delta_T/(2s^{1/2})]\}, \tag{3.4}$$

where

$$\Delta_T = \Delta_{DD}/\sqrt{2} + \Delta_{DA}, \tag{3.5}$$

Δ_{DD} being given by Eq. (1.11) and erfc(x) denoting the complementary error function.[6]

With the distribution in Eq. (3.1) the self-consistent equation for $X_{CPA}(s)$, Eq. (2.2), takes the form

$$X_{CPA}(s) = [\pi^{1/2}/\hat{R}(s)]z\exp(z^2)\,\mathrm{erfc}(z), \tag{3.6}$$

in which

$$z = \Delta_{DA}\hat{R}(s)^{1/2}/2[1 - \hat{R}(s)X_{CPA}(s)]^{1/2}. \tag{3.7}$$

Equation (3.6) has two solutions, $X_{CPA}(s) \equiv \hat{R}(s)^{-1}$, and a second, physically meaningful one, which lies below $\hat{R}(s)^{-1}$. We can obtain approximations for the physical solution in the limits $\Delta_{DA}\hat{R}(s)^{1/2} \ll 1$ and $\Delta_{DA}\hat{R}(s)^{1/2} \gg 1$. When $\Delta_{DA}\hat{R}(s)^{1/2} \ll 1$, we find

$$X_{CPA}(s) \approx \pi^{1/2}\Delta_{DA}/2\hat{R}(s)^{1/2}. \tag{3.8}$$

When $\Delta_{DA}/\Delta_{DD} \ll 1$ we have $\hat{R}(s) \approx \hat{R}_0(s)$, in which case Eq. (3.8) leads to a result equivalent to Eq. (1.8). In the opposite limit, $\Delta_{DA}\hat{R}(s)^{1/2} \gg 1$, we can use the asymptotic expansion of erfc(x)[6] to obtain

$$X_{CPA}(s) \approx \hat{R}(s)^{-1}. \tag{3.9}$$

For values of $\Delta_{DA}\hat{R}(s)^{1/2}$ intermediate between these limits, Eq. (3.6) has to be solved numerically. In Fig. 1 we display our results for $X_{CPA}(0)$, which is the negative of the slope of $\ln f(t)$ for $t\Delta_T^2 \gg 1$, as a function of the ratio $\Delta_{DA}/\Delta_{DD} = (n_A\alpha^{1/2}/n_B\beta^{1/2})$. From the figure it is evident that the linear approximation

$$X_{CPA}^{(0)} = \pi^{1/2}\Delta_{DA}/2\hat{R}_0(0)^{1/2} = \tfrac{4}{9}\pi^{7/2}(\alpha\beta)^{1/2}n_A n_D, \tag{3.10}$$

is appropriate only when $\Delta_{DA}/\Delta_{DD} \lesssim 0.5$. On the other hand the approach to the other limiting form, $X_{CPA}(0) = \hat{R}(0)^{-1}$, is slow. For $\Delta_{DA}/\Delta_{DD} = 5$, we calculate $X_{CPA}(0) = 14.8\Delta_{DD}^2$ while $\hat{R}(0)^{-1} = 16.6\Delta_{DD}^2$. For $\Delta_{DA}/\Delta_{DD} = 8$, the corresponding numbers are

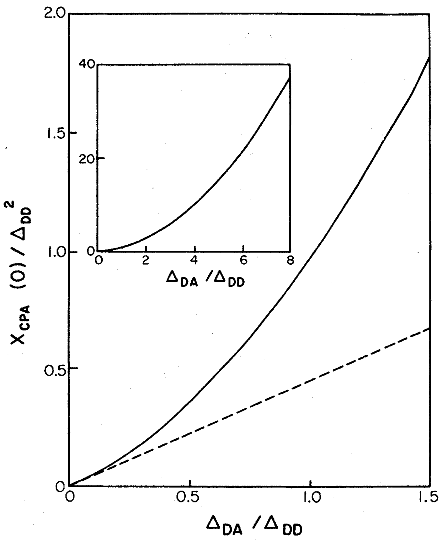

FIG. 1. $X_{CPA}(0)/\Delta_{DD}^2$ vs Δ_{DA}/Δ_{DD}. $X_{CPA}(0)$ is obtained from Eqs. (3.6) and (3.7). The broken line is the linear approximation, Eq. (3.10). The inset shows $X_{CPA}(0)/\Delta_{DD}^2$ for larger values of Δ_{DA}/Δ_{DD}.

$X_{CPA}(0) = 35.8\Delta_{DD}^2$ and $\hat{R}(0)^{-1} = 37.9\Delta_{DD}^2$. Note that, since we have assumed $\alpha \lesssim \beta$, the limit $\Delta_{DA}/\Delta_{DD} \gg 1$ corresponds to $n_A \gg n_B$.

For $\Delta_{DA}/\Delta_{DD} \lesssim 0.1$ the results shown in Fig. 1 are similar to the decay rates obtained from the stochastic model of Burshtein.[11] In the notation of this section, the Burshtein approximation takes the form

$$\hat{f}(s) = [s + X_B(s)]^{-1}. \tag{3.11}$$

The function $X_B(s)$ is given by

$$X_B(s) = \left[\int_0^\infty dt\, e^{-st}\exp\left(\frac{-t}{\hat{R}_0(0)}\right)f_0(t)\right]^{-1} - s - \hat{R}_0(0)^{-1}, \tag{3.12}$$

where we have identified the Burshtein parameter τ_0 with $\hat{R}_0(0)$.[1] Equation (3.12) leads to the same results as the coherent-potential approximation in the limits $\Delta_{DA}/\Delta_{DD} \ll 1$ and $\Delta_{DA}/\Delta_{DD} \gg 1$. However it represents a comparatively crude approximation to the dynamics, and hence is probably less reliable than the CPA for intermediate values of Δ_{DA}/Δ_{DD}.

At present there are relatively few systematic studies of fluorescence at high trap concentration. One of the most detailed is the investigation of the fluorescence from the $^4F_{3/2}$ level in $Nd_xLa_{1-x}F_3$ carried out by Voronko *et al.*[12] In this system the transfer takes place via the electric dipole interactions. The neodymium ions also acts as traps through the mechanism of cross relaxation. By examining various features of the decay curves, they were able to infer that $\alpha \approx 0.01\beta$. Since each ion can serve as either an acceptor or a donor, n_A is equal to n_D. As a result the ratio Δ_{DA}/Δ_{DD} has the value 0.1. From Fig. 1 we conclude that for this value of the ratio the linear approximation gives satisfactory results. According to Eq. (3.10), the limiting decay rate is equal to $\frac{4}{9}\pi^{7/2}(\alpha\beta)^{1/2}n_{Nd}^2$, n_{Nd} being the concentration of Nd ions. As discussed in Ref. 12, the experimental decay rates were found to be proportional to the square of the neodymium concentration, in agreement with our analysis.

IV. DISCUSSION

The results presented in this paper provide a basis for the interpretation of fluorescent-decay curves in dilute systems with dipole-dipole transfer from donors to acceptors and between donors. Using standard numerical techniques, it is a relatively straightforward matter to obtain solutions to Eq. (3.6) and hence determine $\hat{f}(s)$. The behavior of $f(t)$ in the time domain can be inferred by inverting the corresponding Laplace transform. Although it is beyond the scope of this paper to discuss $f(t)$ in detail for all values of time, following Ref. 12, we can identify three limiting regimes. For $0<t<t_1$ the decay is exponential in time

$$f(t)=\exp(-At)\,; \tag{4.1}$$

for $t_1<t<t_2$, $f(t)$ varies according to

$$f(t)=\exp(-Bt^{1/2})(\text{dipole-dipole transfer})\,; \tag{4.2}$$

and for $t>t_2$, $f(t)$ evolves into the asymptotic form discussed in this paper

$$f(t)\exp[-X_{CPA}(0)t]\,. \tag{4.3}$$

Equations (4.1) and (4.2) have a simple physical interpretation. They are the short- and long-time limits of the Inokuti-Hirayama equation for $f(t)$, which is valid in the absence of donor-donor transfer[8]

$$f(t)=\prod_l (1-c_A+c_A e^{-X_{ol}t})\,. \tag{4.4}$$

From Eq. (4.4) we identify A with $c_A\sum_l X_{ol}$ and B with $(\frac{4}{3}\pi^{3/2})\alpha^{1/2}n_A$.

We can obtain a rough estimate of t_1 from the equation

$$At_1\approx 1\,, \tag{4.5}$$

whereas t_2 is given by equating the right-hand sides of Eqs. (4.2) and (4.3)

$$t_2=[B/X_{CPA}(0)]^2=9/\pi^4\beta n_D^2\,, \tag{4.6}$$

using the linear approximation for $X_{CPA}(0)$.

Implicit in the analysis of Secs. I–III is the assumption that back transfer from the acceptors to the donors can be neglected. In the Appendix, it is shown that, in an approximation where the off-diagonal elements of the t matrix are neglected, which is equivalent to assuming that each acceptor interacts with a single donor, the effect of back transfer can be taken into account by the replacement $X_{ol}\to X_{ol}^{eff}(s)$, where the effective transfer rate is given by

$$X_{ol}^{eff}(s)=\frac{X_{ol}(s+\gamma_A)}{s+\gamma_A+\hat{X}_{ol}}\,, \tag{4.7}$$

where γ_A^{-1} is the radiative lifetime in the trap, and $\hat{X}_{ol}$ is the back transfer rate from the acceptor to the donor. The latter is related to X_{ol} through the detailed balance condition

$$\hat{X}_{ol}=e^{-\Delta/k_BT}X_{ol}\,, \tag{4.8}$$

where Δ is the energy difference between donor and acceptor levels.

As noted, the theory applied only to systems with comparatively slow donor-acceptor transfer ($\alpha\lesssim\beta$). The development of an analogous theory for systems where $\alpha\gg\beta$ remains an unsolved problem. Finally, we mention that a central theme of this paper, as in I, is the close formal connection between fluorescent decay in the presence of a random distribution of traps and the electronic states of disordered alloys. In a certain sense fluorescent decay is an example of the behavior of a disordered system in the time domain, whereas the density of states in the alloy problem mirrors disorder in the frequency domain.

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APPENDIX

In this appendix we discuss the behavior of $f(t)$ when allowance is made for back transfer from the traps. We consider the situation $c_A\ll 1$ where the average t matrix approximation is applicable. In this case we can treat the interaction of an array of donors located at sites l with a single acceptor at site o. The relevant rate equations are

$$\frac{dP_l}{dt}=-\Big(\sum_{l'}W_{ll'}+X_{ol}\Big)P_l(t)+\sum_{l'}W_{ll'}P_{l'}(t)+\hat{X}_{ol}P_A(t) \tag{A1}$$

and

$$\frac{dP_A(t)}{dt} = -\left(\gamma_A + \sum_l \hat{X}_{0l}\right) P_A(t) + \sum_l X_{0l} P_l(t) . \tag{A2}$$

Here $P_A(t)$ denotes the probability that the trap is filled at time t, γ_A^{-1} is the "radiative lifetime" of the trap, and $\hat{X}_{0l}$ is the rate of transfer from the trap to the donor at site l. The latter is related to the donor-acceptor transfer rate X_{0l} by the detailed balance equation (4.8).

Combining the Laplace transforms of Eqs. (A1) and (A2) we obtain the result

$$s\hat{P}_l(s) - P_l(0) = -\left(\sum_{l'} W_{ll'} + X_{0l}\right)\hat{P}_l(s) + \sum_{l} W_{ll'}\hat{P}_{l'}(s) + \hat{X}_{0l}\sum_{l'} X_{0l'}(s+\gamma_A+\hat{X}_T)^{-1}\hat{P}_{l'}(s) , \tag{A3}$$

where $\hat{X}_T = \sum_l \hat{X}_{0l}$ is the total back transfer rate.

From Eq. (A3) we infer that the t matrix for the problem obeys the equation

$$t_{ll'}(s) = V_{ll'}(s) - \sum_{l'',l'''} V_{ll''} g_{l''l'''}(s) t_{l'''l'}(s) , \tag{A4}$$

where the nonlocal interaction $V_{ll'}$ is given by

$$V_{ll'} = X_{0l}\delta_{ll'} - \hat{X}_{0l} X_{0l'}(s+\gamma_A+\hat{X}_T)^{-1} . \tag{A5}$$

If the acceptor interacts with a single donor located at l we have

$$t_{ll'} = \frac{X_{0l}^{\mathrm{eff}}(s)\delta_{ll'}}{1 + X_{0l}^{\mathrm{eff}}(s) g_0(s)} , \tag{A6}$$

where the effective donor-acceptor transfer rate is given by

$$X_{0l}^{\mathrm{eff}}(s) = X_{0l}(s+\gamma_A)/(s+\gamma_A+\hat{X}_{0l}) , \tag{A7}$$

which is the same as Eq. (4.7).

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

[2] With a finite lower limit we obtain instead $\hat{f}(s) = (s + (\frac{2}{3}\pi^2) n_A [\alpha/\hat{R}_0(s)]^{1/2}\{1-(2/\pi)\tan^{-1}[r_c^6/\alpha\hat{R}_0(s)]^{1/2}\})^{-1}$.

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