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On the direct energy transfer via exchange to randomly distributed acceptors

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This paper investigates the direct, incoherent energy transfer due to exchange from an excited donor to randomly distributed acceptors. Making use of a general, exact formula for the time and concentration dependent ensemble averaged decay [Blumen and Manz, *J. Chem. Phys.* **71**, 4694(1979)] simple approximate expressions for the limiting cases, of low and high concentrations and of short and long times, also under the inclusion of the back-transfer in the pair approximation, are derived; for low acceptor concentrations and long times the results of Inokuti and Hirayama [*J. Chem. Phys.* **43**, 1978 (1965)] generalized to arbitrary dimensions, are retrieved. The limits of validity of the different approximations are determined by a numerical evaluation of the exact formula for particular lattices of interest.

I. INTRODUCTION

This article studies the *direct* incoherent energy transfer from a donor to randomly distributed acceptors under the assumption that the microscopic transfer rate from the donor to a particular acceptor depends *exponentially* on distance. In the case of excitons, as pointed out by Dexter,¹ such a dependence arises readily, if the donor-acceptor interaction is due to exchange; by now it is accepted that triplet exciton transfer results from the exchange interaction.²⁻⁸ Furthermore, the expressions derived in the following can also be applied to electron scavenging problems, where the rate of transfer of the electron to a particular scavenger depends exponentially on the mutual distance.⁹⁻¹¹

Given that the exponential dependence of the microscopic transfer times on distance is a common occurrence, we extend here the treatment of a previous work (Blumen and Manz, Ref. 12) to include this kind of behavior. In Ref. 12, a general, ensemble averaged expression for the time evolution of the excitation of a donor, surrounded by randomly distributed acceptors, was derived; the formula obtained is valid for all times, for an arbitrary number of different acceptor species, and for all acceptor concentrations. The general expression was applied to the case of multipolar interactions (which depend on distance according to a power law); it allowed a transparent rederivation of the approximate, low concentration, Förster-Dexter decay behavior,^{1,13-15} also generalized to arbitrary dimensions^{16,17}; it also permitted one to establish the limits of validity of the approximate expressions, by comparing these to the exact decay curves, evaluated numerically for several lattices of interest.¹²

Here we evaluate the exact expression for the exchange case also including back transfer in the pair approximation. For exchange interactions, the approximate decay behavior, valid at low acceptor concentration and for long times, was determined by Inokuti and Hirayama in the three-dimensional case¹⁸ and was extended to arbitrary dimensions by Blumen and Silbey.¹⁹ The use of the exact expression allows us to show explicitly the assumptions inherent in the derivation of the

approximate formulas and to establish their regions of validity. Also, the influence of the lattice becomes evident; for short range interactions, it leads in the intermediate time region to the appearance of a wavy pattern superimposed on the smooth decay.

The paper is structured as follows: In Sec. II, the assumptions of the model are stated and the exact decay formula is presented and discussed. Section III studies the properties of the ensemble averaged decay function for the exchange interaction and derives analytical approximations valid for limiting cases. In Sec. IV, the numerical results obtained by directly evaluating the formula are shown. These are compared to the expressions of Sec. III and to the decay behavior obtained with the multipolar interactions in Ref. 12. Section V summarizes the findings.

II. THE ENSEMBLE AVERAGED DECAY FUNCTION

The starting point of our considerations is an excited donor molecule (for convenience assumed to be centered at the origin) which is surrounded by randomly distributed acceptor molecules. A typical realization of this situation is the case that the acceptors occupy substitutional sites in a host material. We assume first that the acceptors, which may be of A different types, are restricted to N sites, and that the probability of a molecule of type α ($\alpha = 1, \dots, A$) to occupy one of the sites i ($i = 1, \dots, N$) is p_α (independent of i). Also, we neglect any acceptor-acceptor interactions.

Since the intramolecular (radiational and radiationless) decay channels of the donor are to a very good approximation independent of the energy transfer mechanism, their inclusion leads to a simple factor $\exp(-t/\tau_D)$, with τ_D^{-1} the rate of intramolecular energy decay, which multiplies the decay law ϕ due to the energy transfer. Thus, we will in the following center our attention on the decay function ϕ .

Let us start with a single donor-acceptor pair. We denote by $w(\mathbf{R}_i)$ the energy transfer rate from the donor to the acceptor, where \mathbf{R}_i is the position of the acceptor. Typical forms of $w(\mathbf{R}_i)$ are

$$w(\mathbf{R}_i) = \frac{1}{\tau} \left(\frac{d}{R_i} \right)^s \quad (2.1)$$

for isotropic multipolar interactions and

$$w(\mathbf{R}_i) = \frac{1}{\tau} \exp[\gamma(d - R_i)] \quad (2.2)$$

for isotropic exchange interactions.¹ Equations (2.1) and (2.2) are expressed in terms of d , the next-neighbor distance, and of τ^{-1} , the transfer rate from a donor to an acceptor at distance d . The use of the forms (2.1) or (2.2) assumes, of course, that the transfer time is longer than the phonon relaxation time so that any excess energy is randomized on the time scale of the transfer. For quantitative statements regarding a particular experiment, the proper form of $w(\mathbf{R}_i)$, which, in general, may be different from the idealized Eqs. (2.1) and (2.2), must be used.

For the donor-acceptor pair, the time evolution of the donor excitation under the influence of $w(\mathbf{R}_i)$ is

$$E_i(t) = \exp[-tw(\mathbf{R}_i)] \quad (2.3a)$$

if back transfer to the donor is neglected, and

$$\tilde{E}_i(t) = \exp[-tw(\mathbf{R}_i)] \cosh[tw(\mathbf{R}_i)] \quad (2.3b)$$

if the direct and the back transfer rates are equal.

Expressions (2.3a) and (2.3b) are obtained as solutions to the differential equations

$$\frac{d}{dt} E_i(t) = -w(\mathbf{R}_i) E_i(t), \quad (2.4a)$$

$$\begin{aligned} \frac{d}{dt} \tilde{E}_i(t) &= -\frac{d}{dt} [1 - \tilde{E}_i(t)] \\ &= -w(\mathbf{R}_i) \tilde{E}_i(t) + w(\mathbf{R}_i) [1 - \tilde{E}_i(t)], \end{aligned} \quad (2.4b)$$

respectively; in Eq. (2.4b), $1 - \tilde{E}_i(t)$ is the time evolution of the excitation of the acceptor. As an example, Eq. (2.4a) holds if the excited level of the acceptor lies lower than that of the donor by an energy difference much larger than kT . On the other hand, Eq. (2.4b) is appropriate if the donor and the acceptor are of the same chemical species and if their inhomogeneous linewidth is smaller than the thermal energy.

Consider now a particular configuration in which the donor is surrounded by n acceptors occupying some of the N sites, such that n_α molecules of type α ($\alpha = 1, \dots, A$) are present at the sites $i_{\alpha k}$ ($k = 1, \dots, n_\alpha$). This particular configuration will be denoted by \mathbf{K} . In the absence of back transfer from the acceptor to the donor, the decay law is a simple exponential

$$\begin{aligned} \phi(\mathbf{K}; t) &= \exp \left[-t \sum_{\alpha=1}^A \sum_{k=1}^{n_\alpha} w_\alpha(\mathbf{R}_{i_{\alpha k}}) \right] \\ &= \prod_{\alpha=1}^A \prod_{k=1}^{n_\alpha} \exp[-tw_\alpha(\mathbf{R}_{i_{\alpha k}})], \end{aligned} \quad (2.5)$$

where w_α is the decay law corresponding to the molecules of type α . Thus, without back transfer, $\phi(\mathbf{K}; t)$ factorizes according to

$$\phi(\mathbf{K}; t) = \prod_{\alpha=1}^A \prod_{k=1}^{n_\alpha} E_{i_{\alpha k}}(t), \quad (2.6)$$

with $E_{i_{\alpha k}}$ defined according to Eq. (2.3a).

In the case of back transfer in general, the function $\phi(\mathbf{K}; t)$ does not factorize any more. However, one may set as an approximation

$$\tilde{\phi}(\mathbf{K}; t) \equiv \prod_{\alpha=1}^A \prod_{k=1}^{n_\alpha} \tilde{E}_{i_{\alpha k}}(t). \quad (2.7)$$

This corresponds to the repeated exchange of excitation within each donor-acceptor pair.²⁰

What is measured in most experiments of direct energy transfer, however, is not $\phi(\mathbf{K}; t)$ but the global decay function averaged over all configurations

$$\langle \phi(\mathbf{K}; t) \rangle = \sum_{\mathbf{K}} \phi(\mathbf{K}; t) P(\mathbf{K}), \quad (2.8)$$

where $P(\mathbf{K})$ is the probability that configuration \mathbf{K} occurs.

In the case that $\phi(\mathbf{K}; t)$ factorizes [say as in Eqs. (2.6) or (2.7)], the ensemble average (2.8) is exactly (Ref. 12, Appendix)

$$\begin{aligned} \phi(p_0, p_1, \dots, p_A; t) &\equiv \langle \phi(\mathbf{K}; t) \rangle \\ &= \prod_{i=1}^N \sum_{\alpha=0}^A p_\alpha E_{i_\alpha}(t). \end{aligned} \quad (2.9)$$

In Eq. (2.9), p_α is the probability with which molecules of type α are distributed on the different sites and $p_0 = 1 - \sum_{\alpha=1}^A p_\alpha$ is the probability that the sites are occupied by host molecules. Also, the $E_{i_\alpha}(t)$ denote the pairwise time evolutions and we have set $E_{i_0}(t) \equiv 1$. One should note that in Eq. (2.9) [distinct from Eqs. (2.6) or (2.7)] the product extends over all sites.

One verifies most readily that Eq. (2.9) holds by expanding the product on its right hand side¹²; one then obtains a sum of all the different $\phi(\mathbf{K}; t)$ functions, each weighted with its proper coefficient $P(\mathbf{K})$.

Equation (2.9) takes a more familiar form if one restricts it to a single acceptor species:

$$\begin{aligned} \phi(p; t) &\equiv \phi(1 - p, p; t) = \prod_{i=1}^N [1 - p + p E_{i_1}(t)] \\ &= \prod_{i=1}^N \{1 - p[1 - E_{i_1}(t)]\}. \end{aligned} \quad (2.10)$$

In the case that no back transfer occurs,

$$\phi(p; t) = \prod_{i=1}^N \{1 - p[1 - \exp(-tw(\mathbf{R}_i))]\}, \quad (2.11)$$

which was derived in Refs. 21 and 22. Reference 20 presents also the case of back transfer under the assumption (2.7):

$$\tilde{\phi}(p; t) = \prod_{i=1}^N \{1 - p[1 - \exp[-tw(\mathbf{R}_i)] \cosh[tw(\mathbf{R}_i)]]\}. \quad (2.12a)$$

Although physically different, Eqs. (2.11) and (2.12a) are formally equivalent, as may be seen by rewriting the latter in the form

$$\tilde{\phi}(p; t) = \prod_{i=1}^N \left[1 - \frac{p}{2} \{1 - \exp[-2tw(\mathbf{R}_i)]\} \right]. \quad (2.12b)$$

One has only to make the change $p \rightarrow p/2$; $t \rightarrow 2t$ in Eq. (2.11) in order to obtain from the results without back

transfer also the back transfer results under the pair assumption [Eq. (2.7)]:

$$\tilde{\phi}(p;t) = \phi(p/2;2t). \quad (2.12c)$$

Up to now no restrictions were imposed on the N sites, which were largely arbitrary. In the numerical evaluation of Sec. IV, however, we take the sites to be distributed on four different lattices: face centered cubic (fcc), planar triangular, square, and linear. The products on the right hand sides of Eqs. (2.10)–(2.12) are absolutely convergent; thus, for an infinite lattice, for example, Eq. (2.11) takes the form

$$\phi(p;t) = \prod_i' (1 - p\{1 - \exp[-tw(\mathbf{R}_i)]\}), \quad (2.13)$$

where the product runs over all lattice sites with the exception of the origin. In Sec. IV, lattices of different dimensions are considered, since, as pointed out in Refs. 12 and 19, a convenient way to simulate strongly anisotropic interactions in three dimensions is to use the isotropic decay laws (2.1) and (2.2) restricted to spaces of lower dimensionality. First, however, we present in the next section analytical approximations to the exact decay function in the exchange case.

III. THE DIRECT DECAY LAW FOR EXCHANGE INTERACTIONS

In this section, we study the properties of the function $\phi(p;t)$ in the case that the microscopic energy transfer law is governed by the exchange interaction. Let us first consider the simple case showing the salient features; it is given by assuming a single acceptor species, an infinite, regular lattice, and no back transfer. From Eqs. (2.13) and (2.2), one has therefore

$$\phi(p;t) = \prod_i' \left\{ 1 - p \left[1 - \exp\left(-\frac{t}{\tau} \exp[\gamma(d - R_i)]\right) \right] \right\}. \quad (3.1)$$

Taking the logarithm of both sides of Eq. (3.1) allows one to rewrite the expression as a power series in $p^{12,22}$:

$$\ln \phi(p;t) = - \sum_{k=1}^{\infty} \frac{p^k}{k} S_k(t), \quad (3.2)$$

with

$$S_k(t) = \sum_i' \left[1 - \exp\left(-\frac{t}{\tau} \exp[\gamma(d - R_i)]\right) \right]^k. \quad (3.3)$$

In Eq. (3.1), the logarithmic terms were expanded in a series and the order of summation interchanged, which is allowed, since the sums are absolutely convergent. The idea behind the expansion (3.2) is that it leads readily to the low concentration expressions for $\phi(p;t)$. If we assume p to be very small ($p \ll 1$), we can approximate the sum in Eq. (3.2) by its first term

$$\ln \phi(p;t) \approx -p \sum_i' \left[1 - \exp\left(-\frac{t}{\tau} \exp[\gamma(d - R_i)]\right) \right]. \quad (3.4)$$

Using now the continuum approximation, we replace the sum in Eq. (3.4) by an integral. The proper transformation for a Δ -dimensional lattice is

$$\sum_i' h(R_i) \rightarrow \Delta \cdot V_{\Delta} \cdot \rho \int_0^{\infty} h(R) R^{\Delta-1} dR. \quad (3.5)$$

In the last expression, V_{Δ} is the volume of a unit sphere in a space of Δ dimensions, b is a cutoff parameter, of the order of d , that accounts for the exclusion of the origin from the sum on the left hand side, and ρ is the density of lattice points in the particular lattice considered. For instance, ρ is d^{-1} for a linear chain, d^{-2} for a square lattice, $(2/\sqrt{3})d^{-2}$ for a triangular and $\sqrt{2}d^{-3}$ for a fcc lattice.

Setting $S_k^{\Delta c}(t)$ for $S_k(t)$ evaluated according to the prescription (3.5), one obtains

$$\begin{aligned} S_1^{\Delta c}(t) &= \Delta V_{\Delta} \rho \int_b^{\infty} \left[1 - \exp\left(-\frac{t}{\tau} \exp[\gamma(d - R)]\right) \right] R^{\Delta-1} dR \\ &= V_{\Delta} \rho \gamma^{-\Delta} g_{\Delta}\left(\frac{t}{\tau} \exp(\gamma d); \gamma b\right), \end{aligned} \quad (3.6)$$

where we have introduced the auxiliary function

$$g_{\Delta}(u; q) = \Delta \int_q^{\infty} [1 - \exp(-u e^{-y})] y^{\Delta-1} dy. \quad (3.7)$$

The final simplification we now have to make in order to retrieve the results of Refs. 18 and 19 is that the cutoff parameter b is zero. Defining thus

$$g_{\Delta}(u) \equiv g_{\Delta}(u; 0) = \Delta \int_0^{\infty} [1 - \exp(-u e^{-y})] y^{\Delta-1} dy, \quad (3.8)$$

one obtains the final approximate result derived for very low concentrations:

$$\phi_{IH}^{\Delta c}(p;t) = \exp\left[-V_{\Delta} \rho \gamma^{-\Delta} p g_{\Delta}\left(\frac{t}{\tau} e^{\gamma d}\right)\right]. \quad (3.9)$$

The function $g_3(z)$ is identical with the function $g(z)$ introduced by Inokuti and Hirayama,¹⁸ and Eq. (3.9) for $\Delta=3$ is their result [Eq. (23)]. For $\Delta=2$, Eq. (3.9) was given in Ref. 19, using the standard Förster derivation.^{1,13-15} The Appendix summarizes some of the properties of the functions $g_{\Delta}(u)$.

Because of the $d^{-\Delta}$ dependence of ρ , Eq. (3.9) depends only on the product γd , and not on the two parameters independently. The same is true for Eq. (3.1), where the R_i 's may be scaled in terms of d , and R_i/d are constants, depending only on the lattice type.

We now consider the case that the concentration is not very low; then the higher order terms in the p expansion are not negligible anymore. Making use of the continuum approximation, Eq. (3.3) takes the form

$$\begin{aligned} S_k^{\Delta c}(t) &= -\Delta V_{\Delta} \rho \int_b^{\infty} \left\{ \sum_{j=1}^k \binom{k}{j} (-1)^j \right. \\ &\quad \times \left. \left[1 - \exp\left(-\frac{jt}{\tau} \exp[\gamma(d - R)]\right) \right] \right\} R^{\Delta-1} dR \\ &= -V_{\Delta} \rho \gamma^{-\Delta} \sum_{j=1}^k \binom{k}{j} (-1)^j g_{\Delta}\left(\frac{jt}{\tau} \exp(\gamma d); \gamma b\right). \end{aligned} \quad (3.10)$$

In Eq. (3.10), the relation

$$(1 - e^x)^k = - \sum_{j=1}^k \binom{k}{j} (-1)^j (1 - e^{jx}) \quad (3.11)$$

was used. Thus, in the continuum approximation, one has for $\phi(p;t)$ the following expression valid for all concentrations:

$$\phi^{\Delta c}(p;t) = \exp \left\{ V_{\Delta} \rho \gamma^{-\Delta} \sum_{k=1}^{\infty} \left[\frac{p^k}{k} \sum_{j=1}^k \binom{k}{j} (-1)^j \right] \times g_{\Delta} \left(\frac{jt}{\tau} \exp(\gamma d); \gamma b \right) \right\}. \quad (3.12)$$

In the numerical evaluation of the next section, we found it more convenient not to use Eq. (3.12) but to evaluate $\phi(p;t)$ directly from the exact expression [Eq. (2.13)]. Equation (3.12) is, however, very useful in determining approximate analytical forms for $\phi(p;t)$. As an example, we consider now the *short-time* behavior of $\phi(p;t)$ for an arbitrary acceptor concentration.

For small u , $u \ll 1$, one has, from Eq. (3.7),

$$g_{\Delta}(u;q) \approx u \Delta \int_0^{\infty} e^{-y} y^{\Delta-1} dy = u \Delta \Gamma(\Delta, q), \quad (3.13)$$

where $\Gamma(a, x) = \Gamma(a) - \gamma(a, x)$ and $\gamma(a, x)$ is the incomplete gamma function [Ref. 23, Eqs. (6.5.2) and (6.5.3)].

Thus, for $t/\tau \ll \exp(-\gamma d)$,

$$S_k^{\Delta c}(t) = [V_{\Delta} \Delta \rho \gamma^{-\Delta} e^{-\gamma d} \Gamma(\Delta, \gamma b) / \tau] t \delta_{k1} \\ \equiv A_{\Delta} t \delta_{k1} \quad (3.14)$$

since

$$\sum_{j=1}^k \binom{k}{j} (-1)^j j = -k \sum_{j=0}^{k-1} \binom{k-1}{j} (-1)^j = -\delta_{k1}. \quad (3.15)$$

Therefore, for short times, one has for all concentrations an exponential decay law

$$\phi^{\Delta c}(p;t) = \exp(-A_{\Delta} p t), \quad \text{for } t/\tau \ll \exp(-\gamma d). \quad (3.16)$$

In the particular case $p=1$, one obtains, of course, directly from Eq. (3.1) an exponential decay for all times:

$$\phi(1;t) = \prod_i \exp \left(-\frac{t}{\tau} \exp[\gamma(d - R_i)] \right) \quad (3.17)$$

and, in the continuum approximation,

$$\phi^{\Delta c}(1;t) = \exp(-A_{\Delta} t), \quad (3.18)$$

as can be readily seen from the transformation (3.5):

$$\sum_i \left[\frac{1}{\tau} \exp[\gamma(d - R_i)] \right] \rightarrow \frac{1}{\tau} \Delta V_{\Delta} \rho e^{-\gamma d} \int_0^{\infty} e^{-\gamma R} R^{\Delta-1} dR \\ = \frac{1}{\tau} V_{\Delta} \Delta \rho \gamma^{-\Delta} e^{-\gamma d} \Gamma(\Delta, \gamma b) = A_{\Delta}. \quad (3.19)$$

To close this section, we mention the behavior of the decay law under back transfer and also the case of several distinct acceptor species.

For a single acceptor species, with p very small ($p \ll 1$), one has under back transfer from Eqs. (2.12c) and (3.9) the long time behavior

$$\bar{\phi}_{IH}^{\Delta c}(p;t) = \exp \left[-\frac{1}{2} V_{\Delta} \rho \gamma^{-\Delta} p g_{\Delta} \left(\frac{2t}{\tau} e^{-\gamma d} \right) \right]. \quad (3.20)$$

For short times $t/\tau \ll e^{-\gamma d}$, one obtains, from Eqs. (3.16) and (2.12c),

$$\bar{\phi}^{\Delta c}(p;t) = \exp[-A_{\Delta}(p/2)2t] = \phi^{\Delta c}(p;t). \quad (3.21)$$

In this limit, the functions $\bar{\phi}$ and ϕ are therefore identical; this is to be expected since for short times the

concentration of excited acceptors is very low, and the back transfer from the acceptors unimportant.

The case of several acceptor species is of particular significance since it may be used to determine the energy transfer rates to molecules which are isotopically or chemically different; these rates are fundamental parameters of the hopping model, which describes the *indirect* incoherent energy transfer.^{19,24-26} If there are A acceptor species present, and if all p_{α} ($\alpha=1, \dots, A$) are very small, then the decay function [Eq. (2.9)] factorizes¹²:

$$\phi(p_0, p_1, \dots, p_A; t) \approx \prod_{\alpha=1}^A \phi(p_{\alpha}; t), \quad (3.22)$$

so that, for instance, if we consider all interactions to occur in the same space (the extension to spaces of different dimensions is straightforward), one obtains for long times, without back transfer,

$$\phi_{IH}^{\Delta c}(p_0, p_1, \dots, p_A; t) \\ = \exp \left\{ -V_{\Delta} \rho \gamma^{-\Delta} \sum_{\alpha=1}^A \left[p_{\alpha} g_{\Delta} \left(\frac{t}{\tau_{\alpha}} \exp(\gamma_{\alpha} d) \right) \right] \right\}, \quad (3.23)$$

and with back transfer,

$$\bar{\phi}_{IH}^{\Delta c}(p_0, p_1, \dots, p_A; t) \\ = \exp \left\{ -\frac{1}{2} V_{\Delta} \rho \gamma^{-\Delta} \sum_{\alpha=1}^A \left[p_{\alpha} g_{\Delta} \left(\frac{2t}{\tau_{\alpha}} \exp(\gamma_{\alpha} d) \right) \right] \right\}. \quad (3.24)$$

For higher concentrations, however, the factorization (3.22) does not hold anymore, and the expressions become more complex.

We now turn to the numerical evaluation of Eq. (3.1) for particular lattices of interest.

IV. NUMERICAL RESULTS

In this section, the numerical results for the excitation decay law [Eq. (3.1)] are presented for different lattice types and different values of the interaction parameter γd . From these calculations, the domains of validity of the approximate expressions of Sec. III will become evident.

As lattice types, we chose the face centered cubic (fcc), the triangular, the square planar, and the linear chain. The interaction parameter γd is a measure of the range of the interaction and is larger when the exchange interaction [Eq. (2.2)] is of shorter range. We varied this parameter between the values 3 and 10: This choice of γd covers a broad range of interactions and includes the value $\gamma d=5$, which is typical for some molecular crystals of interest.¹⁹ The time was varied between $t = \tau/10$ and $10^6 \tau$ and p between 0.001 and 1.

The general behavior of the decay law is illustrated in Fig. 1 for $\gamma d=5$ and for all lattices considered. As in Ref. 12, we chose to plot $-\ln(-\ln \phi)$ vs $\ln(t/\tau)$. Apart from the fact that such a choice enables a convenient comparison of the results, it also has the advantage of allowing one to present a large range of time values and of emphasizing the decay of the donor in the range 0.9 to 0.1, which might be more accurately monitored experimentally (by measuring the radiational decay) than

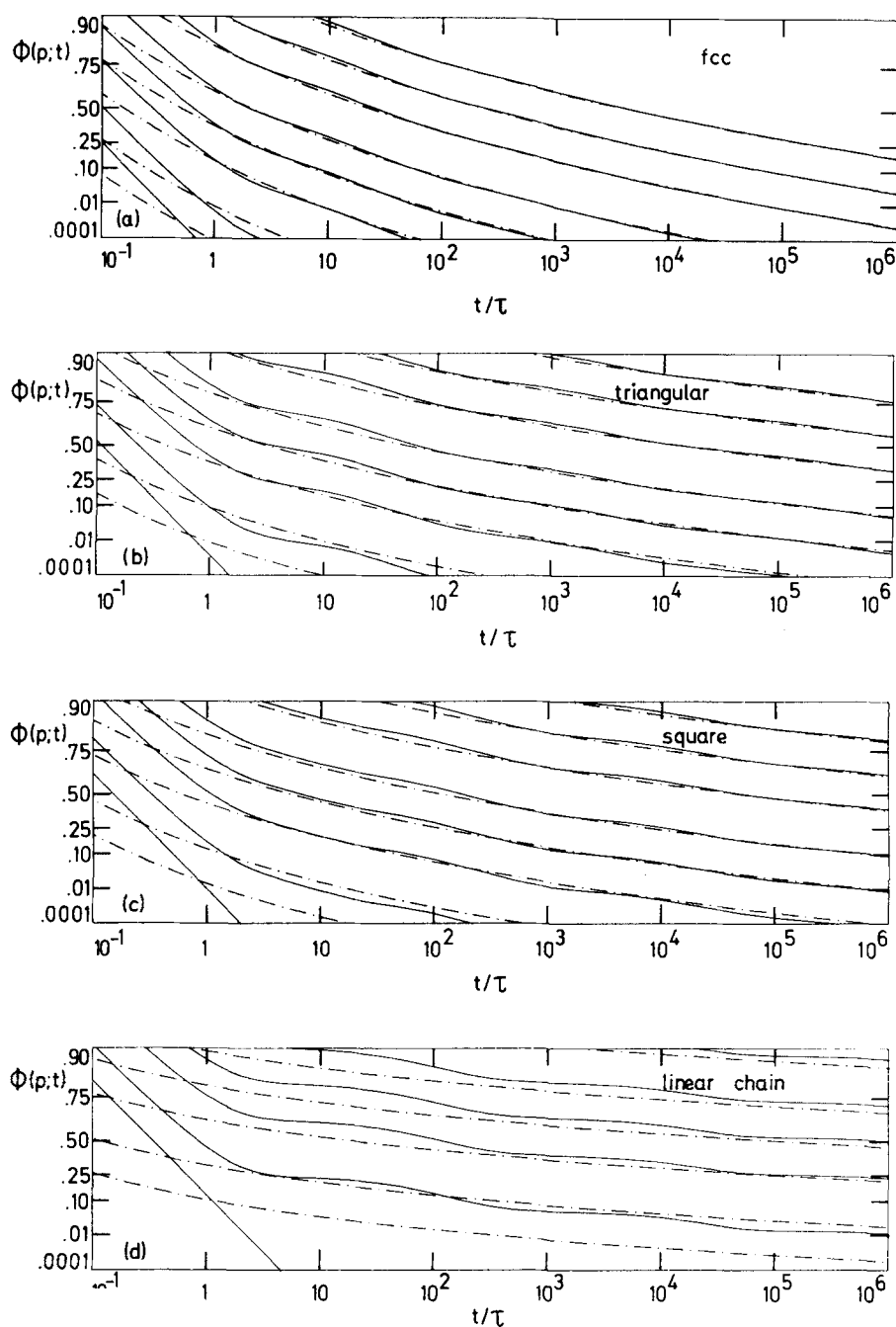


FIG. 1. The time decay of the donor excitation $\phi(p; t)$ due to the direct energy transfer via exchange. The interaction parameter γd equals 5 in all four cases: (a) the fcc lattice, (b) the triangular lattice, (c) the square lattice, and (d) the linear chain. The curves depend parametrically on p ; p is 1.0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, and 0.005 from the left below. The full lines are the exact result, whereas the dash-dot curves are the generalized Inokuti-Hirayama expression [Eq. (3.9)]. Note the $-\ln(-\ln\phi)$ vs $\ln(t/\tau)$ scales.

the region under 0.1 (which corresponds to lower intensities).

Under this choice of scales, an exponential time decay appears as a straight line of slope -1 . From Eq. (3.16), one has

$$-\ln(-\ln\phi^{\Delta c}) = -\ln(t/\tau) + \text{const.} \quad (4.1)$$

so that the domain of validity of Eq. (3.16) for different p and t can be determined directly from Fig. 1, in which the exact decay is plotted as a full curve. Typical is the behavior of the curve corresponding to $p=1$, which is a straight line for all times [as expected from Eq. (3.17)].

For multipolar interactions and long times, one has¹²

$$-\ln(-\ln\phi^{\Delta c}) = -K \ln(t/\tau) + \text{const.} \quad (4.2)$$

with $K = \Delta/s$ and s the interaction parameter ($K \neq 1$). For exchange interactions, the long time behavior of the decay does not follow such a simple pattern; from Eqs. (3.9) and (A12), one has asymptotically

$$\begin{aligned} -\ln(-\ln\phi_{IH}^{\Delta c}) &= -\ln\left[g_{\Delta}\left(\frac{t}{\tau}\right)e^{\gamma d}\right] + \text{const.} \\ &= -\Delta \ln\left[\ln\left(\frac{t}{\tau}\right) + \gamma d\right] + O[\ln^{-1}(t/\tau)], \end{aligned} \quad (4.3)$$

so that the slope of the decay curve tends asymptotically to the horizontal, rather than to a nonzero value (like $-K = -\Delta/s$). For ready comparison to the exact result, we therefore superimpose in Fig. 1 as dash-dot curves

the approximate long-time expression (3.9) evaluated corresponding to the particular lattice.

As is to be expected, Eq. (3.9) is a better approximation of Eq. (3.1) for longer times and for smaller p . However, the quality of the approximation depends also on the interaction parameter γd and on the dimension Δ ; Eq. (3.9) is more adequate for large Δ and for small γd , i. e., for longer-range interactions. This result parallels the findings in the multipolar case, where the Förster–Dexter expressions are very adequate for three dimensional dipolar interactions.¹² Considering now the three dimensional exchange case, the Inokuti–Hirayama result breaks down (as expected) for $0.5 \leq p \leq 1$; however, for $\gamma d = 5$, it holds quite well for p as large as 0.2 and for t already slightly larger than the energy transfer time to nearest neighbors, a result not readily expected considering the rough approximations involved in deriving Eq. (3.9) from (3.1).

As in the multipolar case, the exact curves show a wavy pattern superimposed on the smooth overall decay; this pattern gets more prominent for smaller Δ and for larger γd values, and is due to the lattice structure.¹²

The four cases shown in Fig. 1 have the same parameter $\gamma d = 5$. In order to be able to present succinctly results for other γd values, we plot in Fig. 2 τ_e , the time at which the donor is still excited with probability $1/e$, as a function of p . The time τ_e is the $1/e$ decay time of Inokuti and Hirayama¹⁸ and is given implicitly by $\phi(p; \tau_e) = 1/e$. In the case of energy migration, τ_e may be used to define the hopping time.^{24,25} In Fig. 2, the presented curves depend parametrically on γd . As in Fig. 1, the exact results are drawn as uninterrupted and the approximate results as dash–curves. Note that we plot both τ_e and p logarithmically.¹²

For large p , τ_e/τ turns out to be small so that we expect Eq. (3.16) to hold. Therefore, for $p \leq 1$,

$$\ln(\tau_e/\tau) \approx -\ln p - \ln A_\Delta \quad (4.4)$$

and the shape of the exact curves should be linear with slope -1 , for all Δ and γd . This is indeed well fulfilled, as can be seen from Fig. 2. For exchange interactions, the small p behavior of the $\tau_e(p)$ functions is different from the multipolar case; the slope of $\tau_e(p)$, plotted as in Fig. 2, does not tend asymptotically to a finite limit. On the other hand, for multipolar interactions,¹² the asymptotic slope is $-s/\Delta$.

To facilitate the comparison with the approximate expression (3.9), we plotted the functions $\tau_e(p)$ evaluated from it in Fig. 2 as dash–dot curves. The comparison leads to analog findings as the analysis of Fig. 1: The generalized Inokuti and Hirayama expression is a better approximation for the face centered cubic than for the other lattices; its quality decreases in the following lattice series: triangular, square, and linear. Also, the expression lies nearer to the exact result if γd is smaller, i. e., if the microscopic interactions are of longer range. As one sees from Fig. 2(a), for $\gamma d = 3$ and $\tau_e \geq 1$, Eq. (3.9) leads to a very adequate description of the $\tau_e(p)$ dependence.

However, one should note that, for times shorter than 0.5τ , the formula (3.9) breaks down even *qualitatively*; the curves corresponding to the approximate expression cross; taking this result seriously would imply that, for the same configurations and the same transfer rate to the acceptors in next neighbor position, the transfer is more rapid for *shorter-range* interactions, which is evidently a wrong result. Indeed, the exact time decay curves and the exact $\tau_e(p)$ solutions do not cross. Comparing the $1/e$ decay times found here with the multipolar results of Ref. 12, one observes readily the difference in shape due to the different asymptotic behavior of $\tau_e(p)$ for long times and small concentrations, as discussed above. Given, however, that concentration changes are more difficult to monitor experimentally than time changes, the diagnostic decision if a particular direct energy transfer is of multipolar or of exchange type may be more readily taken from the asymptotic differences of the two cases as given in Fig. 1, which correspond to measurements of the decay law in the time domain.

A short remark to the wavy pattern superimposed on the smooth decay is necessary: It is due to the lattice structure; as in the multipolar case, the points of inflexion of the steep portions of the $\tau_e(p)$ curves are given approximately by¹²

$$p_j = 1 - \exp(-1/\nu_j),$$

where ν_j is the total number of lattice points enclosed by each lattice shell, where a shell is defined as the set of lattice points equidistant to the origin. For the linear chain, i. e., $\nu_j = 2j$, $p_1 = 0.39$ and $p_2 = 0.22$. For the triangular lattice, $p_1 = 0.15$ and $p_2 = 0.08$; for the square lattice, $p_1 = 0.22$ and $p_2 = 0.12$; and for the fcc lattice, $p_1 = 0.08$. The importance of the superimposed wavy feature increases in the series fcc, triangular, square, and linear.

V. CONCLUSIONS

In this paper, under the model assumption of the direct transfer from one donor to randomly distributed acceptors, the exchange mediated energy transfer was studied by means of an exact expression for the ensemble averaged decay. In this sense, the time and concentration dependent formulas of Sec. II and the numerically evaluated curves presented in Sec. IV are exact solutions of the model; the results are valid for the whole range of concentrations and times.

As we have shown in Sec. II, the inclusion of back transfer within the framework of the pair approximation is also a simple matter; the back transfer results can be directly read off from the decay curves in the absence of back transfer, through a change of variables, whereby the concentration parameter is halved, and the time is doubled [Eq. (2.12c)].

The general exact formula enabled us in Sec. III to retrieve the approximate formulas of Inokuti and Hirayama¹⁸ for the exchange induced excitation decay, which had been derived by the Förster–Dexter formalism^{1,13–15} and are thus valid for long times and low acceptor concentrations. We have also obtained the extension of

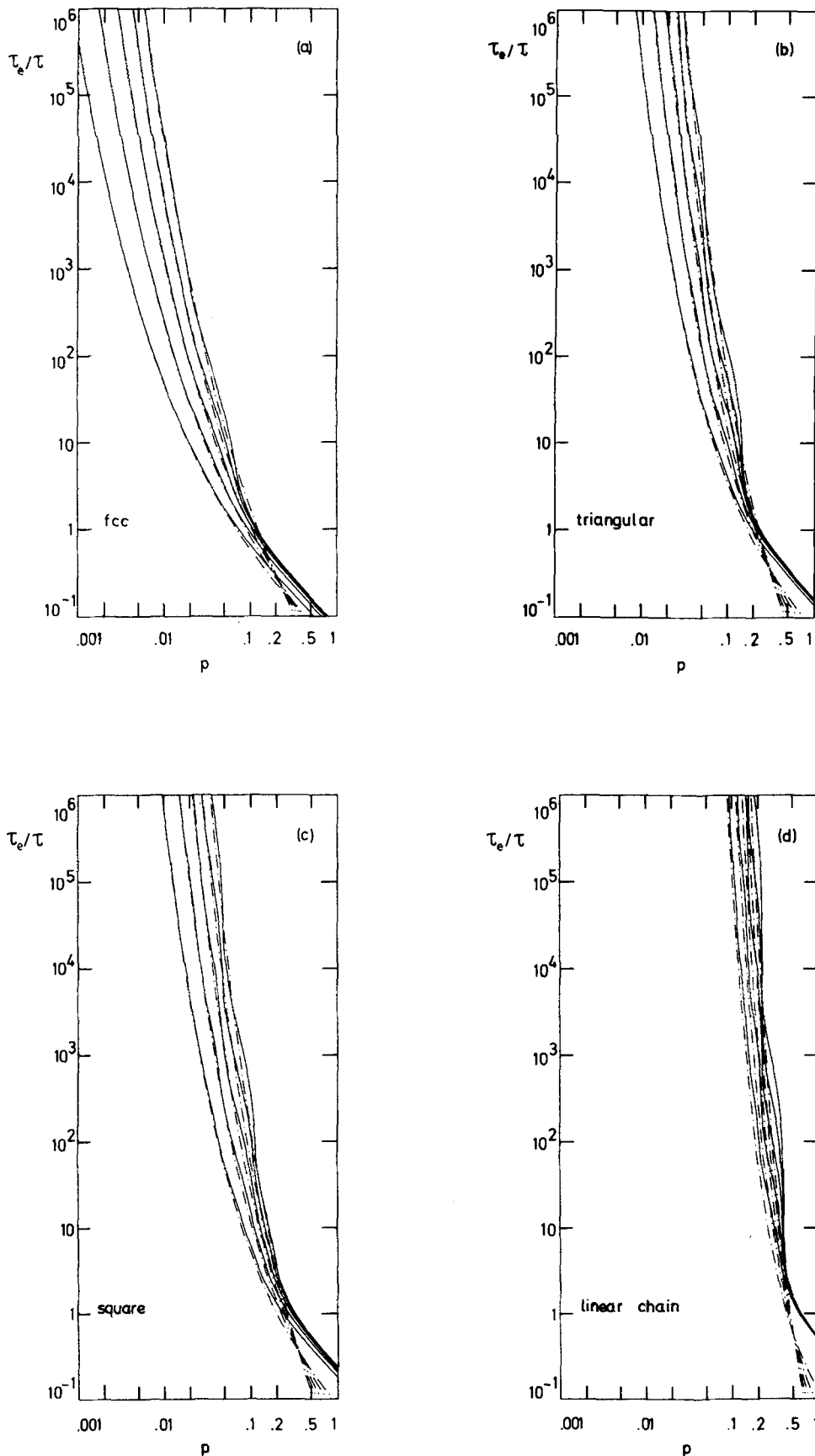


FIG. 2. The time τ_e ($1/e$ decay time, at which the donor is still excited with probability $1/e$), as a function of p . Shown are (a) the fcc lattice, (b) the triangular lattice, (c) the square lattice, and (d) the linear chain. The curves depend on the interaction parameter γd , which is 3, 4, 5, 6, and 7, in order from the left below. Again the full lines are the exact result, whereas the dash-dot lines are approximate, corresponding to Eq. (3.9). Note the $\ln(\tau_e/\tau)$ vs $\ln p$ scales.

these expressions to interactions in spaces of different dimensions. Since all these formulas are the first term in a series expansion in the powers of concentration, one can use in applications the continuum approach of Sec. III to choose from the complete series that analytical approximate expression, which is accurate to the degree needed.

In Sec. IV, we determined the range of validity of the approximate results¹⁸ by comparing them to the exact solutions. For long range interactions in three dimensions, the approximate expressions hold quite well even for relatively high acceptor concentrations of the order of 10% and for times larger than the transfer time to next neighbors. Caution, however, must be exercised; the quality of the low concentration approximation gets worse for shorter-range interactions and for lower dimensionality; also, if the time decreases, the approximation ceases to be valid even *qualitatively* and the breakdown occurs quite abruptly.

Comparison of the exchange mediated transfer to the transfer via multipolar interactions also shows, besides some common features, characteristic differences. The long time asymptotic behavior of the decay curves plotted as $-\ln(-\ln\phi)$ vs $\ln(t/\tau)$ is markedly different: In the multipolar case, they reach a nonzero slope, depending on dimensionality and interaction law, whereas the slope in the exchange case tends to zero. Correspondingly, the two cases differ in the dependence of the $1/e$ decay times on concentration. The common features include the fact that the small concentration expressions approximate better the behavior of the decay curves for isotropic three dimensional long-range interactions and that the underlying lattice structure leads to the superposition of a wavy pattern on the smooth decay law; this pattern can be directly related to the lattice structure around the donor molecule.

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APPENDIX: THE FUNCTION $g_{\Delta}(u)$

In Sec. III the function $g_{\Delta}(u)$ was defined through

$$g_{\Delta}(u) \equiv \Delta \int_0^{\infty} [1 - \exp(-u e^{-y})] y^{\Delta-1} dy, \quad \text{for } \Delta \neq 0. \quad (\text{A1})$$

From this expression, one obtains after integrating by parts the following equivalent forms:

$$g_{\Delta}(u) = u \int_0^1 \exp(-ux) (-\ln x)^{\Delta} dx, \quad (\text{A2})$$

$$g_{\Delta}(u) = \int_0^u \exp(-x) (\ln u - \ln x)^{\Delta} dx. \quad (\text{A3})$$

We start our considerations from Eq. (A1), from which one readily has the following series expansion:

$$g_{\Delta}(u) = \sum_{j=1}^{\infty} \frac{(-1)^{j-1} u^j}{j!} \Delta \int_0^{\infty} \exp(-jy) y^{\Delta-1} dy \\ = \Delta! \sum_{j=1}^{\infty} \frac{(-1)^{j-1} u^j}{j! j^{\Delta}} = \Delta! u \sum_{i=0}^{\infty} \frac{(-u)^i}{i! (i+1)^{\Delta+1}}. \quad (\text{A4})$$

Equation (A4) leads directly to the recurrence formula

$$u \frac{d}{du} g_{\Delta}(u) = \Delta g_{\Delta-1}(u), \quad (\text{A5})$$

from which the $g_{\Delta}(u)$ can be obtained as repeated integrals by observing that

$$g_{\Delta}(0) = 0, \quad \text{for all } \Delta \quad (\text{A6})$$

and

$$g_0(u) = 1 - e^{-u}.$$

Thus,

$$g_{\Delta}(u) = \Delta! \int_0^u \frac{du_{\Delta}}{u_{\Delta}} \dots \int_0^{u_3} \frac{du_2}{u_2} \int_0^{u_2} \frac{du_1}{u_1} (1 - e^{-u_1}). \quad (\text{A7})$$

As a special case, we obtain

$$g_1(u) = C_E + \ln(u) - Ei(-u), \quad (\text{A8})$$

where $Ei(x)$ is the exponential integral [Ref. 27, Eq. (8.211)] and C_E is the Euler constant.

The asymptotic behavior of $g_{\Delta}(u)$ for large u may be evaluated from Eq. (A3), by expanding $g_{\Delta}(u)$ in powers of $\ln u$:

$$g_{\Delta}(u) = \sum_{j=0}^{\Delta} \binom{\Delta}{j} (-1)^j (\ln u)^{\Delta-j} \int_0^u e^{-x} (\ln x)^j dx. \quad (\text{A9})$$

The integrals appearing on the right hand of Eq. (A9) are the derivatives of the incomplete gamma function $\gamma(a, u)$ [Ref. 23, Eq. (6.5.2)] at $a = 1$:

$$\gamma(a, u) \equiv \int_0^u e^{-x} x^{a-1} dx, \quad (\text{A10})$$

$$\left. \frac{d^j \gamma(a, u)}{da^j} \right|_{a=1} = \int_0^u e^{-x} (\ln x)^j dx. \quad (\text{A11})$$

For large u , the incomplete gamma function may be approximately replaced by the gamma function, thus obtaining¹⁸

$$g_{\Delta}(u) \approx \sum_{j=0}^{\Delta} \binom{\Delta}{j} (-1)^j \Gamma^{(j)}(1) (\ln u)^{\Delta-j}. \quad (\text{A12})$$

The derivatives of the gamma functions are connected to the polygamma functions $\psi^{(n)}(z)$ through

$$\psi^{(n)}(z) = \frac{d^{n+1}}{dz^{n+1}} \ln \Gamma(z) \quad (\text{A13})$$

[Ref. 23, Eq. (6.4.1)]. One obtains therefore, up to constant terms,

$$g_1(u) \approx \ln u + 0.57722 = \ln u + C_E, \\ g_2(u) \approx \ln^2 u + 1.15443 \ln u + 1.97811, \\ g_3(u) \approx \ln^3 u + 1.73165 \ln^2 u + 5.93434 \ln u + 5.44487. \quad (\text{A14})$$

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