Regions of applicability of kinematic mechanisms in bimolecular processes

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The relative decrease in the rate constant for exchange and multipole quenching as compared with the value estimated by the diffusion theory is calculated by the encounter theory method for arbitrary migration lengths $0<\lambda_0<\infty$. The feasibility of extrapolating the diffusion and jump solutions to intermediate λ_0 by means of formulas which join them to the mixed quenching mechanism is investigated. The black sphere model, which describes the diffusion and hopping limits to lowest order, is shown to be invalid for intermediate λ_0.

1. INTRODUCTION

Random walks of electrons or excitons with a finite migration length λ_0 are accompanied by trapping in liquid and solid solutions. The trapping rate constant was originally calculated by Smolukhovskiĭ (cf. Ref. 1) for the case when $\lambda_0 \to 0$, i.e., when the random walk can be approximated by continuous diffusion. He also assumed that trapping is certain to occur once the particle enters a "black sphere" of radius R_s surrounding the trap, and that no trapping occurs outside this sphere. The phenomenological black sphere model is now widely employed; it defines the trapping rate as the frequency kc of encounters with traps, where c is the density of the traps,

$$k=4\pi R_s D, \qquad (1.1)$$

and D is the encounter diffusion coefficient. This theory is essentially the same as the ones developed later in Refs. 2–4, which merely determine the dependence of R_s on D and define the black sphere radius R_s more precisely in terms of the probability $w(r)$ for an electron or exciton to reach a trap.

However, the diffusion approximation for the approach to a trap is not always correct. The transport probability $w(r)$ falls off so rapidly with distance that the characteristic diameter of the strong interaction region in which trapping is certain is usually comparable to or even less than λ_0. In this case only a single "hop" is needed to take the particle into the strong interaction region, and the diffusion description becomes invalid. However, the black sphere formalism may also be useful in this case; the radius R_w of the spheres is now determined by the hopping frequency τ_0^{-1} rather than by $D=\lambda_0^2\tau_0^{-1}$. The black sphere model yields[5,6]

$$k=\frac{4\pi}{3}R_w^3\tau_0^{-1} \qquad (1.2)$$

for the quenching rate constant associated with hopping; the dependences of the rates k in (1.1) and (1.2) on the electron or exciton migration rates and transport constants are generally different.

Equations (1.1) and (1.2) are valid for $\lambda_0\to 0$ and $\lambda_0\to\infty$, respectively, and remain approximately correct even for finite λ_0 if we neglect corrections of order λ_0 and λ_0^{-1} in the diffusion and hopping cases, respectively. However, there is a large intermediate region in which neither formula is valid. In order to judge the success of the black sphere approximation in the diffusion and hopping limits and for intermediate values λ_0, it will therefore be of interest to analyze the relatively few cases in which the problem admits an exact solution for arbitrary λ_0 without recourse to the black sphere formalism.

Such a program was first carried out in Ref. 7 for migration of self-stabilized electrons in a liquid (the Torrey model[8]). The interest in Ref. 7 was primarily in the "exchange" mechanism of trapping, whose probability decays exponentially with distance:

$$w(r)=w_0\exp(-2r/L). \qquad (1.3)$$

In the binary trap approximation, the problem reduces to solving an integral equation which has a kernel of a specific form. This equation characterizes the hopping length distribution for average hopping times and lengths equal to τ_0 and λ_0, respectively. The general expression for the rate constant is

$$k=4\pi R_Q D, \qquad (1.4)$$

where the effective trapping radius R_Q depends on τ_0 and λ_0. The ratio R_Q/R_s tends to 1 and 0 in the diffusion and hopping limits, respectively. A "mixed" trapping mechanism for intermediate λ_0 was assumed in Ref. 7, i.e., the rate constant $k=4\pi R_w D$ contained the characteristic parameters for both the diffusion and the hopping limits as multiplicative factors. If this approximation is correct, R_Q/R_s should not decrease monotonically as λ_0 increases from 0 to ∞ but should pass through a low maximum, because R_w is larger than R_s for intermediate λ_0. The situation is exactly the same for trapping (quenching) of an incoherent excitation by the multipole mechanism; in this case the trapping probability decays as a power of the distance,

$$w(r)=c_{DA}/r^m. \qquad (1.5)$$

Although this situation was analyzed semiquantitatively in Ref. 7, the results have been used on several occasions to estimate the quenching rate for intermediate λ_0 for migration of excitations along impurity centers in solid solutions.[9–11]

We emphasize here that the migration mechanisms in

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continuous media are physically distinct from those in solid solutions, and this is reflected in the form of the kernel in the integral describing the random walk, which is considerably more complicated for random walks over a disordered system of centers in a solid. In this case the problem can only be solved numerically. Such a solution was given in Ref. 12 for dipole-dipole migration and quenching. The ratio R_Q/R_s was found to decrease monotonically with decreasing $z = c_{DA}/c_{DD}$, where c_{DD} is the constant for resonant transfer of excitation between identical centers. Since λ_0 increases as z decreases, this result shows that at least for the dipole-dipole interaction, R_Q/R_s has no maximum as λ_0 increases from 0 to ∞.

In the present work we examine the generality of this result and explore its physical origin by means of direct calculations for multipole and exchange quenching in the Torrey model and by using approximate formulas (including first-order corrections in λ_0 and λ_0^{-1}) to extend the solutions into the intermediate region. We calculated R_Q quantitatively for both exchange and multipole quenching by extending the theory developed previously in Ref. 7. We found that the dependence $R_Q/R_s(\lambda_0)$ was in fact monotonic in both cases; moreover, a satisfactory description was achieved by joining the approximate first-order formulas together at the center of the intermediate region. The use of the mixed rate constant for intermediate λ_0 is unjustified because it assumes a greater accuracy than the black sphere model (which is zeroth-order in λ_0) is capable of providing.

2. EXCHANGE QUENCHING OF LUMINESCENCE

The hopping mechanism for electron trapping in liquids was detected experimentally in Ref. 13, where the results were interpreted using Eq. (1.2). Similar behavior was observed in Ref. 14, where electron conduction in chalcogenide glass semiconductors was studied. However, in our context it is preferable to consider trapping of triplet excitations rather than electrons. The migration and trapping (quenching) of triplet excitations both involve the exchange interaction, which like the resonant interaction decays exponentially with distance. The kinematics of migration and trapping are thus identical for electrons and incoherent triplet excitons. By analyzing the quenching of luminescence rather than electron trapping, we will be able to compare the rate constants for quenching of triplet and singlet excitations, i.e., to make comparisons between quenching by the exchange mechanism with probability (1.3) discussed in this section and the multipole quenching given by Eq. (1.5), which we will discuss in Sec. 3.

The encounter theory[7,15] gives the expression

$$k=\int_0^\infty w(r)\,n(r)\,4\pi r^2\,dr, \tag{2.1}$$

for the steady-state quenching rate, where $n(r)$ is the distribution of excitons around an acceptor (which is assumed to occupy a negligible volume). This distribution is described by the integral equation

$$-w(r)\,n(r)-\frac{1}{\tau_0}\left[n(r)-4\pi\int_0^\infty f(r,x)\,n(x)\,x^2\,dx\right]=0, \tag{2.2}$$

whose kernel

$$f(r,x)=\frac{1}{8\pi xr}\left[\Phi(|r-x|)-\Phi(r+x)\right]$$

specifies the probability that an exciton at a distance of x from the acceptor will make a single hop (during an average time τ_0) and enter a spherical shell of radius r. The hopping length distribution in the Torrey model[8] is given by

$$\Phi(z)=\frac{1}{\lambda_0}\exp(-z/\lambda_0); \tag{2.3}$$

here λ_0 is the most probable length, and the mean square displacement is $\lambda^2 = 6\lambda_0^2$. Although the Torrey model corresponds to a definite random walk mechanism, we are interested in it primarily because it admits an exact solution.

An exact solution is possible because the integral equation (2.2) can be reduced to the differential equation

$$\frac{\lambda_0^2}{\tau_0}\frac{d^2}{dr^2}r\eta(r)-\frac{w(r)}{1+w(r)\tau_0}r\eta(r)=0, \tag{2.4}$$

where the function $\eta(r) = n(r)[1 + w(r)\tau_0]$ must be bounded for $r = 0$ and satisfy the obvious boundary condition $\eta(\infty) = n(\infty) = 1$ at infinity. Because $w(r)$ decays with distance at least as rapidly as r^{-3}, η and n both have the same limiting behavior given by the familiar expression $1 - R_Q/R_s$ for large r. This suffices to determine the rate constant (1.4), because the effective quenching radius

$$R_Q=\lim_{r\to\infty} r^2\frac{d}{dr}\eta(r) \tag{2.5}$$

is just the parameter in the asymptotic expansion of η for large r.

The calculation in Ref. 7 gave the result

$$R_Q=\delta[\ln\gamma^2+\xi+2\psi(1/x)+x+G(\xi,x)] \tag{2.6}$$

for exchange quenching (1.3). Here $\delta = L/2$, $\gamma = e^C$ (where C is Euler's constant), $\xi = \ln(w_0\tau_0)$, $x = \lambda_0/\delta$,

$$G(\xi,x)=\frac{\Gamma^2(1/x)F(1/x,1/x,1+2/x;-e^{-\xi})\exp(-\xi/x)}{2\Gamma(2/x)F(-1/x,1/x,1;-e^{\xi})}, \tag{2.7}$$

and $F(\alpha,\beta,\gamma;z)$ is the hypergeometric function of the first kind. This general result describes both the kinetic stage of quenching, which is independent of the relative motion of the partners, and the migration-dominated stage, in which the kinematics of the approach of the partners plays a role. Since we are interested only in the migration-dominated stage, we will confine our attention to the halfplane $\xi > 0$ (Fig. 1), where the quenching is rapid and is therefore limited by the kinematics. We divided the $\xi > 0$ plane into three regions of small, intermediate, and large λ_0 corresponding to the diffusion, mixed, and hopping quenching mechanisms. An adequate estimate for R_Q in the diffusion and intermediate regions can be obtained by setting $G = 0$ in (2.6),

$$R_Q=\delta[\ln\gamma^2+\xi+2\psi(1/x)+x]. \tag{2.8}$$

On the other hand, the formula

$$R_Q=\delta(\xi-x\,\mathrm{th}\,\xi/x). \tag{2.9}$$

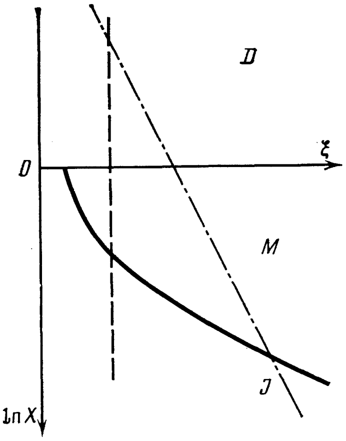

FIG. 1. Boundaries demarcating the migration-controlled quenching mechanisms; D is the diffusion region ($x < 1$); the intermediate region M lies between the ξ axis and the heavy curve, which bounds the hopping region J from above. The vertical and slanted lines correspond to the sections $\tau_0 = \text{const}$ and $D = \text{const}$, respectively.

was derived in Ref. 7 for the intermediate and hopping resions.

A direct numerical calculation using Eqs. (2.6), (2.8), and (2.9) will give complete information regarding the exact solution in any cross section of the region in which it is defined, as well as information on the approximations from above and below (corresponding to the hopping and the diffusion limits). It is natural to take the section defined by $\xi = \text{const}$ as the vertical section (Fig. 2). Since the characteristic parameter τ_0 of the hopping model is constant in this section, it is interesting to choose the other section (Fig. 3) so that $D = \lambda_0^2 \tau_0^{-1} = \text{const}$, i.e.,

$$\xi = 2 \ln x + \ln \frac{w_0 \delta^2}{D}. \tag{2.10}$$

The constant terms $w_0\delta^2/D$ must be large in this section in order for diffusion to dominate the quenching process. We will see below that the exchange and multipole quenchings can be compared only in this section.

We will now analyze the limiting behavior of (2.8) for $x \ll 1$ and $x \gg 1$ and show that for large ξ, the approximations (2.8) and (2.9) completely cover the intermediate region of λ_0 values between the diffusion and hopping limits. For $x \ll 1$, which corresponds to the diffusion limit, we have

$$R_Q = R_s - {}^1/_6 \lambda_0^2/\delta + O(\lambda_0^3/\delta^2), \tag{2.11}$$

and $R_s = \delta[2 \ln(\gamma/x) + \xi]$. For $x \gg 1$ we have

$$R_Q = R_w - \lambda_0 (1 - 1{,}65\delta^2/\lambda_0^2 + O(\delta^3/\lambda_0^2)), \quad \delta < \lambda_0,$$

where $R_w = \delta\xi$. If we expand Eq. (2.9) in the parameter $\xi/x \gg 1$, we get

$$R_Q = R_w - \lambda_0 [1 - 2 \exp(-2R_w/\lambda_0)], \quad \lambda_0 < R_w.$$

The results coincide to lowest order in λ_0:

$$R_Q = R_w - \lambda_0, \quad \delta \ll \lambda_0 \ll R_w. \tag{2.12}$$

This shows that Eqs. (2.8) and (2.9) can be joined at least for values $\delta \ll \lambda_0 \ll R_w$ within the intermediate region (if in fact they do not overlap it completely). For $\xi/x \ll 1$ outside this region, Eq. (2.9) yields the result

$$R_Q = \frac{R_w^3}{3\lambda_0^2}\left[1 - \frac{2}{5}\left(\frac{R_w}{\lambda_0}\right)^2\right], \quad R_w \ll \lambda_0, \tag{2.13}$$

which is valid for the hopping mechanism of quenching.

Numerical calculation confirms that the approximate results (2.8) and (2.9) join together roughly in the center of the intermediate region both for $\tau_0 = \text{const}$ (Fig. 2) for the $D = \text{const}$ (Fig. 3). Figure 3 also shows that they asymptotically approach the curve (2.12) for the mixed mechanism; however, this approach is to opposite branches of the curve and occurs outside the region where (2.12) is valid. In other

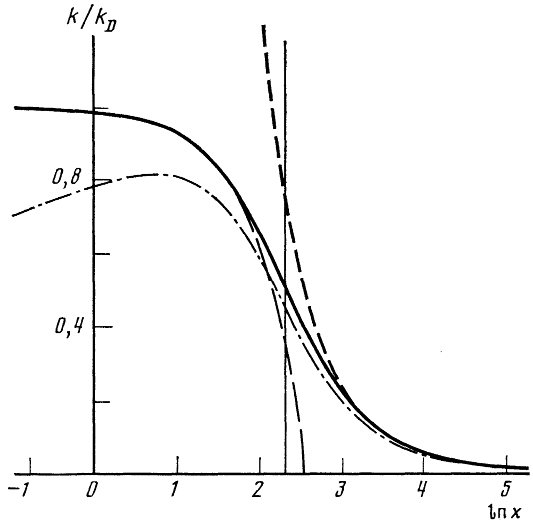

FIG. 2.

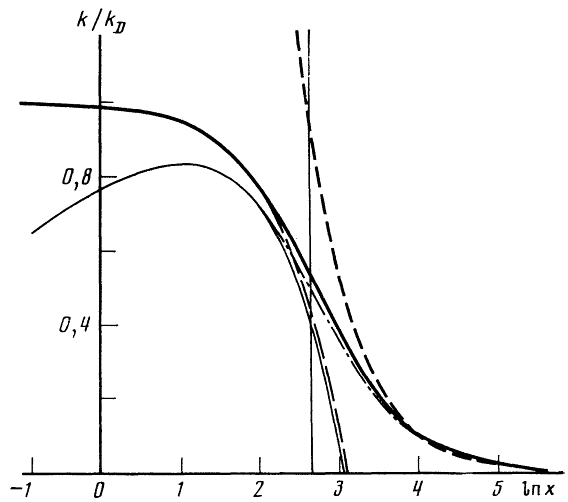

FIG. 3. Relative decrease in the quenching rate constant in the section $D = \text{const}$ [$\ln(w_0\delta^2/D) = 10$]. The vertical line gives the boundary for the hopping mechanism; the veritcal axis $\ln(x) = 0$ gives the boundary for the diffusion regime. The notation is the same as in Fig. 2, except that the light curve shows the approximation (2.12) corresponding to the mixed quenching mechanism.

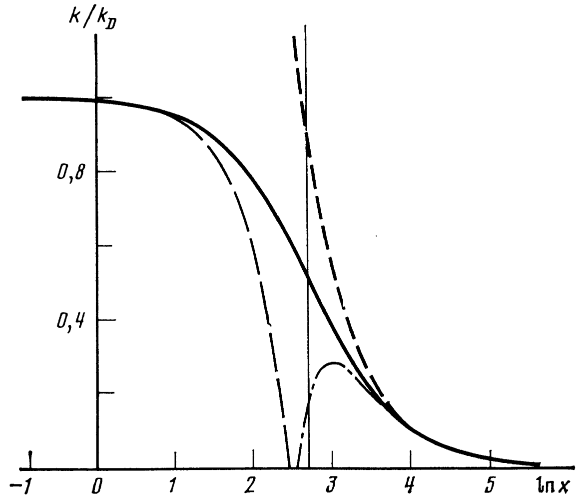

FIG. 4. Approximation of the exact solution shown in Fig. 3 by the approximate formulas (2.11) (long dashes) and (2.13) (dashed-and-dotted curve). Only the lowest-order corrections to the diffusion and hopping descriptions in the black sphere model are included.

words, the mixed quenching mechanism gives an acceptable approximation only in a narrow region where the diffusion and hopping solutions join. The penetration distance of each of the limiting solutions into the mixed region is shown in Fig. 4, where these solutions are replaced by curves showing the behavior of the diffusion and hopping solutions (2.11) and (2.13), which do not join.

Although these results taken together indicate that a mixed quenching mechanism does exist, it is easy to see that the estimate for the effective radius given by the black sphere model is invalid. Indeed, this approximation is correct only for the first terms in (2.11)–(2.13). In the diffusion or hopping limits, we can take λ_0 or λ_0^{-1} to be so small that the correction terms in (2.11) and (2.13) become insignificant; if we neglect them, (1.4) leads to (1.1) or (1.2), respectively. However, the situation is different for intermediate λ_0. Since λ_0 is bounded from below by δ, if we neglect the corrections to R_Q in (1.12) the resulting error will exceed the difference between the effective radii for the diffusion and mixed regimes. In fact, the above discussion implies that

$$R_s=R_w-2\lambda_0\frac{\ln(x/\gamma)}{x}. \tag{2.14}$$

Consequently, for $x\gg1$ in the intermediate region,

$$R_Q=R_w-\lambda_0<R_s<R_w. \tag{2.15}$$

Thus R_Q is less than R_s here; however, if we neglect λ_0, we will have $R_Q\approx R_w$, which is greater than R_s, cf. Fig. 3 in Ref. 7. It might therefore appear that as λ_0 increases from the diffusion to the mixed regimes, the radius and quenching constant should increase. In fact, however, they both decrease monotonically as λ_0 increases; in other words, the black sphere model, which neglects corrections of order λ_0 to the quenching radius, is not valid for intermediate λ_0.

On the other hand, the black sphere model can be used as a first approximation for both the diffusion and the hopping regimes. In addition, this model is convenient because approximate formulas with a straightforward physical interpretation can be used to calculate the radii of the black spheres up to a numerical factor. In the case of diffusion, one requires that the time needed to cross the layer of thickness δ bounding a sphere of radius R_s be long enough to permit complete quenching:

$$w(R_s)\delta^2/D=1. \tag{2.16}$$

Substitution of (1.3) into (2.16) leads to the correct formula for R_s, except that $\gamma=1$ instead of e^C. For the hopping regime, quenching must occur during a single hop while the excitation remains inside a sphere of radius R_w:

$$w(R_w)\tau_0=1. \tag{2.17}$$

If we substitute (1.3) into (2.17), we recover the exact expression for R_w. Of course, this agreement with the exact result is to some extent fortuitous and is a consequence of the rapid decay of the quenching probability $w(r)$ with distance. The numerical discrepancy for multipole (in particular, dipole-dipole) quenching may be large; nevertheless, the functional form of the dependences $R_s(D)$ and $R_w(\tau_0)$ is correctly reproduced, provided the thickness δ of the quenching layer is suitably chosen.

3. MULTIPOLE QUENCHING

We can analyze multipole quenching without altering the kinematics of the random walk by substituting the probability (1.5) into Eq. (2.4). This gives

$$\lambda_0^2\frac{d^2y}{dr^2}-\Phi(r)y=0, \tag{3.1}$$

where $y=r\eta$, and

$$\Phi(r)=\frac{w(r)\tau_0}{1+w(r)\tau_0}=\frac{1}{(r/R_w)^m+1}, \tag{3.2}$$

where $R_w=(c_{DA}\tau_0)^{1/m}$. Since this equation cannot be solved exactly, the quenching rates were only estimated semiquantitatively in Ref. 7 by means of Eqs. (2.16) and (2.17). The previous discussion clearly shows that these estimates are inadequate for intermediate lengths λ_0. We will therefore proceed differently and use the approximation

$$\Phi(r)=\begin{cases}1 & \text{for } r\leqslant R_w, & (3.3a)\\ (R_w/r)^m & \text{for } r>R_w, & (3.3b)\end{cases}$$

which permits an analytic solution. We thus have two regions $r\leqslant R_w$ and $r>R_w$ in which the solutions are different. In the first case, the quenching saturates:

$$y_a=C_a\,\mathrm{sh}\,(r/\lambda_0),\quad r\leqslant R_w, \tag{3.4a}$$

while elsewhere we have

$$y_b=r^{1/2}\{CI_{-\nu}[\varphi(r)]-C_bI_\nu[\varphi(r)]\},\quad r>R_w, \tag{3.4b}$$

with $\phi(r)=2\nu\theta(R_w/r)^{1/2\nu}$ and

$$\theta=R_w/\lambda_0,\quad \nu=(m-2)^{-1}. \tag{3.5}$$

In order to obtain a complete solution of (3.4) valid for all r, we must join the solutions y_a and y_b together with their first derivatives at the point $r=R_w$ and invoke the boundary condition $y_b/r=1$ for y_b as $r\to\infty$, which immediately leads to

$$C=\Gamma(1-\nu)R_w^{1/2}(\nu\theta)^{\nu}.$$

The matching conditions then determine two additional constants, of which we will need only

$$C_b=\left\{I_{-\nu}(2\nu\theta)\left[1-\frac{\operatorname{th}\theta}{2\theta}\right]+\operatorname{th}\theta I_{-\nu}'(2\nu\theta)\right\}$$
$$\times\left\{I_{\nu}(2\nu\theta)\left[1-\frac{\operatorname{th}\theta}{2\theta}\right]+\operatorname{th}\theta I_{\nu}'(2\nu\theta)\right\}^{-1}\Gamma(1-\nu)R_w^{1/2}(\nu\theta)^{\nu}, \tag{3.6}$$

since [cf. (2.5)] the radius can be expressed in terms of Cb as

$$R_Q=C_bR_w^{1/2}(\nu\theta)^{\nu}/\Gamma(1+\nu).$$

The last two formulas give the final expression

$$R_Q=R_w(\nu\theta)^{2\nu}\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\left\{I_{-\nu}(2\nu\theta)\left[1-\frac{\operatorname{th}\theta}{2\theta}\right]\right.$$
$$\left.+\operatorname{th}\theta I_{-\nu}'(2\nu\theta)\right\}\left\{I_{\nu}(2\nu\theta)\left[1-\frac{\operatorname{th}\theta}{2\theta}\right]+\operatorname{th}\theta I_{\nu}'(2\nu\theta)\right\}^{-1}. \tag{3.7}$$

The matching conditions cause both the modified Bessel functions I_ν and their derivatives I_ν' to appear in the result (here the primes denote derivatives with respect to the arguments). The parameter ν characterizes the steepness of the multipole quenching (regarded as $L/2$-exchange), and the correspondence among the remaining quantities is established by setting $\xi/x=0$.

It is clear from the preceding that the inequality $\theta\gg1$ rules out the hopping mechanism of quenching. However, this does not suffice to justify using the diffusion limit, which in this case requires that

$$\nu\theta\gg1. \tag{3.8}$$

Indeed, when (3.8) holds we can use the asymptotic expansion for the Bessel functions in (3.7) to get

$$R_Q=R_w(\nu\theta)^{2\nu}\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\left[1-\frac{1}{2\nu\theta}\left(\nu+\frac{1}{2}\right)e^{-4\nu\theta}\sin\pi\nu\right]. \tag{3.9}$$

On the other hand, in the hopping limit when

$$\nu\theta<\theta\ll1, \tag{3.10}$$

expansion of (3.7) with respect to the small parameters leads to

$$R_Q=R_w\theta^2\frac{m}{3(m-3)}\left[1-\frac{2m-1}{5m}\theta^2\right]$$
$$=R_w\theta^2\frac{1+2\nu}{3(1-\nu)}\left[1-\frac{2+3\nu}{5(1+2\nu)}\theta^2\right]. \tag{3.11}$$

For $\nu\ll1$, the regions defined by (3.8) and (3.10) are separated by a gap $\nu R_w\ll\lambda_0\ll R_w$ in which the quenching may be regarded as mixed. The correction terms in (3.9) and (3.11) make it possible to extrapolate the results for the diffusion and hopping mechanisms to intermediate λ_0.

If these corrections are neglected, we recover the familiar formula[16]

$$R_Q=R_s=\nu^{2\nu}\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\left(\frac{R_w^{2+1/\nu}}{\lambda_0^2}\right)^{\nu}=\nu^{2\nu}\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\left(\frac{c_{DA}}{D}\right)^{\nu}; \tag{3.12}$$

for diffusion quenching; moreover, the radius for the hopping regime

$$R_Q=\frac{m}{m-3}\frac{R_w^3}{3\lambda_0^2} \tag{3.13}$$

coincides with its exchange analog, apart from a numerical factor.

These results can be derived (up to the numerical factors found above) from Eqs. (2.16) and (2.17), respectively, if we take

$$\delta=\nu R_s. \tag{3.14}$$

This formula refines the definition $\delta=R_s/m$ given in Ref. 7 for the thickness of the quenching layer bounding the black sphere. Formula (2.16) for calculating $R_s(D)$ is radically different from the formula $w(R_s)R_s^2/3D=1$ suggested previously in Refs. 17 and 18. The latter formula assumes that quenching occurs throughout the time the excitation is contained inside the black sphere; in fact, however, only the time needed to diffuse across the boundary layer of the sphere (of thickness δ) is relevant, because the excitation is completely quenched inside this layer. This can be seen clearly from Fig. 5, which plots the exciton flux $J=-4\pi r^2Ddn/dr$ reaching an acceptor as a function of the relative distance r/R_0 from the acceptor; the gradient ∇J, which gives information on the spatial distribution of the quenching, is also shown.

In view of the definition (3.14), we can now introduce the quantities $x=\lambda_0/\delta$ and

$$\xi=R_w/\delta=(m-2)x^{2/m}, \tag{3.15}$$

which are identical to the ones used in Sec. 2. We see from (3.15) that x and ξ are uniquely related for multipole quenching, regardless of whether D or τ_0 is assumed to vary while the other is constant. The radius R_Q calculated from the general formula (3.7) gives complete information regarding the gradual transition from diffusion to hopping quenching as x increases (Fig. 6). Although the interval of x values separating these two extremes is quite wide, the lowest-order corrections for the finiteness of λ_0 in (3.9) and (3.11) enable us to extend the solution roughly as far as the midpoint of the intermediate region. There is thus no need to derive the analogs of (2.8) and (2.9) for multipole quenching. If we compare Figs. 4 and 6, we see that the qualitative behavior for multi-

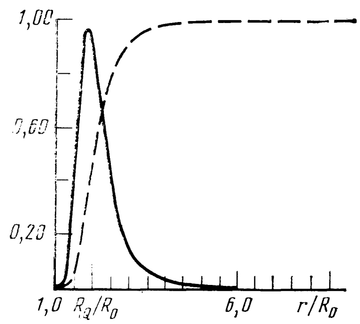

FIG. 5. Normalized exciton diffusion flux $J(R)/J(\infty)$ toward an acceptor (dashed curve) and its derivative (solid curve), which reflects the spatial distribution of the quenching; $m=10$ and R_0 is the distance of closest approach.

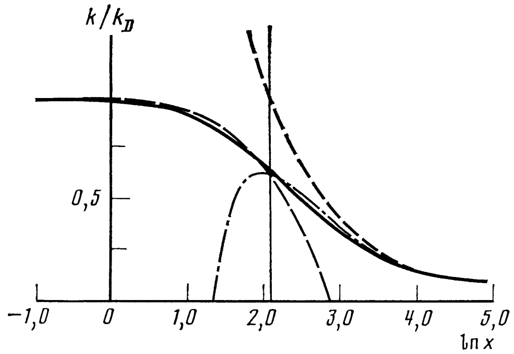

FIG. 6. Change in the rate constant for dipole-dipole quenching as the length of an elementary hop increases (heavy curve). The approximations given by Eqs. (3.9) and (3.11) (dashed and dashed-and-dot curves, respectively) are also shown; only the lowest-order corrections are included.

pole and exchange quenching is the same. The quenching rate can be calculated adequately by the black sphere model for both the diffusion and the hopping limits, provided the sphere radii are given by Eqs. (2.16) and (2.17). However, the leading corrections to the black sphere approximation must be included in order to describe the quenching for intermediate λ_0, and the transition from the diffusion to the hopping regimes can be established only through exact calculations. Although this transition is accompanied by a monotonic decrease in R_Q/R_s which is characteristic for each type of interaction, the qualitative behavior is apparently independent of the details of the interaction and of how the migration occurs. In any case, the behavior is similar to that found in Ref. 12 for dipole quenching in the case of migration over a disordered system of centers with quasiresonant dipole-dipole energy transfer.

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