Exact asymptotics for nonradiative migration-accelerated energy transfer in one-dimensional systems

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We study direct energy transfer by multipolar or exchange interactions between diffusive excited donor and diffusive unexcited acceptors. Extending over the case of long-range transfer of an excitation energy a nonperturbative approach by Bray and Blythe [Phys. Rev. Lett. **89**, 150601 (2002)], originally developed for contact diffusion-controlled reactions, we determine exactly long-time asymptotics of the donor decay function in one-dimensional systems.

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I. INTRODUCTION

Long-range nonradiative transfer of an excitation energy from excited donor molecules to acceptors of the excitation energy is a dominant reaction mechanism in various chemical, physical, and biological processes [1–5]. To name but a few, we mention fluorescence, luminescence, or phosphorescence quenching, decay of trapped electrons in glassy media in the presence of scavengers, or light harvesting by antennae chlorophyll-b molecules, and donation of singlet energy to the chlorophyll-a reaction centers in photosynthetic organisms.

The idea of direct nonradiative transfer has been put forward in the pioneering works of Förster [6] and Dexter [7], who determined decay of an immobile excited donor due to dipole-dipole interactions with immobile, randomly placed acceptors in rigid three-dimensional solutions. Subsequent analysis (see Refs. [8] and references therein) extended the consideration of Förster and Dexter to arbitrary Euclidean dimensions d and to general forms of donor-acceptor interactions, such as isotropic multipolar interactions, for which the rate $W(r)$ of energy transfer is given by

$$W(r) = \alpha_m \left(\frac{r_0}{r} \right)^n , \tag{1}$$

or interactions mediated by exchange, for which one has

$$W(r) = \alpha_e \exp(-\gamma r), \tag{2}$$

where r is the distance separating a given donor-acceptor pair, the constants n, r_0, and γ determine the interaction type and range (e.g., $n=6$ for dipolar, $n=10$ for quadrupolar interactions).

Note that an exponential form in Eq. (2) emerges, as well, in another important area—outer sphere electron transfer reactions. Kinetics of such electron tunneling processes taking place in liquids or glassy media have been also widely studied giving rise to a very beneficial cross-fertilization of ideas and approaches.

For the transfer rates in Eqs. (1) and (2), it was found [8] that the probability $P(t)$ that the donor is still in an excited state up to time t obeys, at sufficiently long times,

$$P(t) \sim \exp[-V_d \Gamma(1-d/n) n_A r_0^d (\alpha_m t)^{d/n}] \tag{3}$$

for multipolar and

$$P(t) \sim \exp[-V_d \gamma^{-d} n_A \ln^d(\alpha_e t)] \tag{4}$$

for exchange-mediated transfer, respectively. In Eqs. (3) and (4), n_A denotes mean density of acceptor molecules, $V_d = \pi^{d/2}/\Gamma(1+d/2)$ and $\Gamma(x)$ is a gamma function. The decay forms in Eqs. (3) and (4) have been also generalized for certain types of restricted geometries—fractals [9], porous [4,9–11] and various microheterogeneous [12] media, as well as polymer solutions [13,14].

However, in many situations the donors and acceptors are not immobile. In liquids, both donor and acceptor molecules perform diffusive motion. In solids, excitations become delocalized because of incoherent hopping between donor sites, which ultimately results in a diffusive transport, although the decay kinetics may be still different from that predicted for conventional diffusive motion—there always exists a finite probability that an excitation remains on an intitially excited donor [15,16].

It was recognized [17] that random migration of donor and acceptor molecules leads to a much more efficient deactivation than the direct transfer between the immobile species; in three-dimensions, in particular, one finds that $P(t)$ obeys [17]

$$P(t) \sim \exp[-4\pi(D_A + D_D) R_{\text{eff}} n_A t], \tag{5}$$

where D_D and D_A are donor and acceptor diffusion coefficients and R_{eff} is the effective reaction radius.

Note that the result in Eq. (5) has been first obtained for $W(\rho)$ in Eq. (1) with $n=6$ and $D_A=0$ in Ref. [18], which analyzed the relaxation of the nuclear magnetization in the

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presence of paramagnetic impurities. Recently, the result in Eq. (5) has been generalized to three-dimensional (3D) systems with donors and acceptors performing anomalous, "fractional" diffusion [19].

To the best of our knowledge, there do not exist analogous results for low-dimensional, (i.e., 1D and 2D) systems, although the extension of the approach of Refs. [17] for 1D and 2D situations seems to be straightforward. In doing so, one will find

$$P(t) \sim \exp[-n_A \phi(t)], \tag{6}$$

where $\phi(t) \sim [(D_A+D_D)t]^{1/2}$ in 1D and $\phi(t) \sim (D_A+D_D)t/\ln[(D_A+D_D)t]$ in 2D.

On the other hand, it is clear that neither Eq. (5) nor Eq. (6) is an exact solution for the long-range energy transfer problem involving diffusive donor and acceptor molecules, but a result of a certain assumption. While particles' diffusion coefficients will indeed appear only in the form of a sum D_A+D_D in the solution of a problem with a single donor and a single acceptor, it is not the case in the general situation with a concentration of acceptor molecules. In particular, setting $D_A=0$, one should obtain a crossover to a singular behavior characterized by a stretched-exponential time dependence $\ln P(t) \sim -t^{d/(d+2)}$ [20], whereas Eq. (5) does not show any singularity in the limit $D_A \to 0$.

Apart of this, it was recently discovered [21] that, remarkably, for diffusion-controlled contact $C+B \to B$ reactions taking place in low dimensional systems (or, generally, in dimension $d \leqslant d_f$, where d_f is the fractal dimension of particles' trajectories in case of subdiffusive motion [23]), the long-time asymptotical form of $P(t)$ is *independent* of the C particle diffusion coefficient.

In this paper we extend the nonperturbative approach of Bray and Blythe [21] developed originally for contact diffusion-controlled reactions to systems with diffusive donor and acceptors interacting via distance-dependent isotropic multipolar or exchange transfer rates in Eqs. (1) and (2). We define, in the form of convergent in the limit $t \to \infty$ upper and lower bounds, the exact form of the excitation survival probability $P(t)$ in one-dimensional systems. More specifically, we show that in 1D systems, both for multipolar and exchange-mediated transfer $P(t)$ obeys

$$1 + O\left(\frac{1}{t^{1/2}}\right) \leqslant \frac{\ln P(t)}{-4n_A\sqrt{D_A t/\pi}} \leqslant 1 + O\left(\frac{1}{t^{1/6}}\right). \tag{7}$$

This exact result proves that, in contrast to predictions based on standard considerations, Eq. (6), the donor decay function in 1D is independent of the donor's diffusion coefficient in the asymptotic regime. Remarkably, the decay forms appear to be *exactly* the same as for *contact* diffusion-controlled trapping reactions (such that reaction takes place upon encounters between particles), [21] despite the fact that in our case reaction proceeds via *long-range* transfer rates in Eqs. (1) and (2) and encounters between particles do not lead to any particular reaction event.

In a separate publication [24], we proceed to show that this is also true for two-dimensional systems, while in 3D one may obtain a fluctuation-induced lower bound on the decay function which, in some range of parameters, is better (higher) than predictions based on the standard Smoluchowski approach, Eq. (5).

This paper is outlined as follows. In Sec. II we define the model and introduce basic notations for the general d-dimensional case. In Sec. III we derive a general upper bound on the global decay function, while Sec. IV presents the derivation of the lower bound. Next, in Secs. V and VI, focusing on a 1D case, we evaluate the bounds on the global decay functions eplicitly for exchange-mediated and multipolar transfer, respectively, and demonstrate that they coincide in the asymptotic limit $t \to \infty$ defining in such a way an asymptotically exact result. Finally, in Sec. VII we conclude with a brief recapitulation of our results and an outlook for future work.

II. MODEL AND BASIC EQUATIONS

Consider a d-dimensional spherical volume V containing a single excited donor molecule, which is initially located at the origin, and K acceptor molecules, placed at random positions. Suppose that both donor and acceptors perform conventional diffusive motion with diffusion coefficients D_D and D_A, respectively. Let the instantaneous positions of the donor and of the acceptors be denoted by the (d-dimensional) vectors $\mathbf{r}(t)$ and $\mathbf{R}_k(t)$, $k=1,2,\ldots,K$.

We will neglect here the backtransfer to the donor. This neglect is well-justified if the donor-acceptor energy difference is much larger than k_BT, T being temperature and k_B the Boltzmann constant. We also disregard here donor-specific radiative and radiationless processes. These decay channels are independent of the direct energy transfer and thus the overall donor decay function factorizes into the product of the donor-specific decay law, $\exp(-t/\tau_R)$, where τ_R is the rate of the donor-specific decay, times the acceptor determined decay function. Thus we focus here only on the nonradiative donor-acceptor transfer.

One assumes the acceptors to act independently, which means that they contribute multiplicatively to the decay. This assumption is well-fulfilled when the density of acceptors is low. Under such an assumption, the probability that the donor is still in an excited state at time t, for a given realization of its trajectory $\mathbf{r}(t)$ and given realizations of acceptors' trajectories $\{\mathbf{R}_k(t)\}$, is given by

$$P[\mathbf{r}(t),\{\mathbf{R}_k(t)\}] = \prod_{k=1}^{K} \exp\left[-\int_0^t W(\rho_k(t'))dt'\right], \tag{8}$$

where ρ_k denotes the separation distance between the donor and kth acceptor.

Experimentally measured property is the global decay function averaged over all possible donor and acceptor trajectories

$$P(t) = E_0^D\left\{\left\langle \prod_{k=1}^{K} E^A_{\mathbf{R}_k(0)}\left\{\exp\left[-\int_0^t W[\rho_k(t')]dt'\right]\right\}\right\rangle_{\mathbf{R}_k(0)}\right\}, \tag{9}$$

where the symbol $E_0^D\{\cdots\}$ denotes averaging with respect to all possible donor's trajectories $\mathbf{r}(t)$; symbols $E^A_{\mathbf{R}_k(0)}\{\cdots\}$ de-

note averaging with respect to the trajectories of the kth acceptor, commencing its motion at position $\mathbf{R}_k(0)$, and finally, the angle brackets stand for the averaging with respect to the distribution of the starting positions. Note that presenting $P(t)$ in the form as in Eq. (9), we have already implicitly assumed that all acceptors move independently of each other, which is again well-justified for sufficiently low acceptor concentrations.

After some straightforward calculations, we arrive at the following thermodynamic-limit expression:

$$P(t) = E_0^D\{\exp[-n_A Q[\mathbf{r}(t);t]]\}, \tag{10}$$

where n_A is the mean concentration of acceptor molecules ($n_A = K/V$ when both $K, V \to \infty$), while $Q[\mathbf{r}(t);t]$ is the following functional of a given donor trajectory $\mathbf{r}(t)$:

$$Q[\mathbf{r}(t);t] = \int d\mathbf{R}(0) E^A_{\mathbf{R}(0)}\left\{1 - \exp\left[-\int_0^t dt' W[|\mathbf{r}(t') - \mathbf{R}(t')|]\right]\right\}. \tag{11}$$

In the latter equation, $\mathbf{R}(t)$ denotes a given trajectory of a single acceptor molecule and $E^A_{\mathbf{R}(0)}\{\cdots\}$ denotes averaging over all possible trajectories $\mathbf{R}(t)$. Note that straightforward averaging in Eqs. (10) and (11) is a nontractable mathematical problem since averaging over acceptor trajectories in Eq. (11) has to be taken first for a *given* realization of the donor's trajectory and only after doing it, one may perform averaging of the exponential in Eq. (10). Consequently, a recourse has to be made to approximations.

III. UPPER BOUND ON THE GLOBAL DECAY FUNCTION: PASCAL PRINCIPLE

A convenient for our purposes upper bound on the global decay function stems from the so-called Pascal principle, which in our terms can be formulated as follows: an excitation on an immobile donor molecule survives longer than on a randomly moving one. In other words, $P(t)$ in Eq. (10) is bounded by

$$P(t) \leqslant P_u(t), \tag{12}$$

where $P_u(t)$ describes the decay of an immobile donor, fixed at the origin, due to a concentration n_A of *diffusive* acceptor molecules,

$$P_u(t) = \exp\left[-n_A \int d\mathbf{R}(0) \times E^A_{\mathbf{R}(0)}\left\{1 - \exp\left(-\int_0^t dt' W[|\mathbf{R}(t')|]\right)\right\}\right]. \tag{13}$$

The inequality in Eq. (12) looks very plausible on physical grounds but appears quite difficult to prove. It has been first conjectured in [21] for contact trapping reactions and proven in Ref. [22] for one-dimensional systems. In Ref. [25] [in which Eq. (12) has been named "Pascal principle" paraphrazing in mathematical terms a statement of Pascal that "all misfortune of man comes from the fact that he does not stay peacefully in his room"], this inequality has been proven for a rather general class of random walks on d-dimensional lattices. We also remark that a similar statement has been proven earlier in Ref. [15] for the process of an excitation energy migration via distance-dependent transfer rates on a disordered array of immobile donor molecules and quenched by randomly placed immobile acceptors. It was shown that the survival probability of an excitation can be only decreased because of random motion not correlated with acceptors' spatial distribution. However, no rigorous proof of such a statement exists at present for diffusion-controlled long-range reactions although it is intuitively clear that the inequality in Eq. (12) should hold in this case too. We thus assume, without proof, that the inequality in Eq. (12) is also valid for the model under study.

Next, applying Feynmann-Kac theorem [27,28] one may show that

$$E^A_{\mathbf{R}(0)}\left\{\exp\left[-\int_0^t dt' W[|\mathbf{R}(t')|]\right]\right\} = \int d\mathbf{R} G_t[\mathbf{R}|\mathbf{R}(0)], \tag{14}$$

$G_t[\mathbf{R}|\mathbf{R}(0)]$ being the Green's function solution of the following reaction-diffusion equation:

$$\frac{\partial}{\partial t} G_t[\mathbf{R}|\mathbf{R}(0)] = D_A \Delta_{\mathbf{R}} G_t[\mathbf{R}|\mathbf{R}(0)] - W(|\mathbf{R}|) G_t[\mathbf{R}|\mathbf{R}(0)],$$

$$G_{t=0}[\mathbf{R}|\mathbf{R}(0)] = \delta[\mathbf{R} - \mathbf{R}(0)], \tag{15}$$

where $\Delta_{\mathbf{R}}$ is a d-dimensional Laplace operator.

Note that Eqs. (15) presume that donor and acceptors are pointlike, noninteracting particles. In reality, they possess hard cores and cannot approach each other at a distance less than a, equal to the sum of donor and acceptor radii. This means that Eqs. (15) are to be complemented by a reflective boundary condition at $|\mathbf{R}| = a$ [2].

Taking advantage of Eqs. (14) and (15), we can formally rewrite Eq. (13) as

$$P_u(t) = \exp\left[n_A \int_0^t dt' \int d\mathbf{R} \frac{\partial G_{t'}(\mathbf{R})}{\partial t'}\right],$$

$$G_t(\mathbf{R}) = \int d\mathbf{R}(0) G_t[\mathbf{R}|\mathbf{R}(0)]. \tag{16}$$

Assuming next that $G_t(\mathbf{R})$ is independent of angular variables such that $G_t(\mathbf{R}) = G_t(r)$, where $r = |\mathbf{R}|$, we get the following compact expression:

$$P_u(t) = \exp\left[-n_A \int_0^t dt' k_u(t')\right], \tag{17}$$

in which equation $k_u(t)$ is determined by

$$k_u(t) = dV_d \int_a^\infty r^{d-1} W(r) G_t(r), \tag{18}$$

and $G_t(r)$ obeys

$$\frac{\partial G_t(r)}{\partial t} = D_A\left(\frac{\partial^2 G_t(r)}{\partial r^2} + \frac{d-1}{r}\frac{\partial G_t(r)}{\partial r}\right) - W(r)G_t(r),$$

$$G_{t=0} = 1; \quad G_t(r\to\infty) = 1, \quad \left.\frac{\partial G_t(r)}{\partial r}\right|_{r=a} = 0. \quad (19)$$

Equations (17)–(19) thus define the upper bound on the global decay function $P(t)$ in systems with diffusive donor and acceptors.

IV. LOWER BOUND ON THE GLOBAL DECAY FUNCTION

We turn now to the derivation of a lower bound on $P(t)$ in Eq. (10). Following Ref. [21] (see also Ref. [26]), we make the following steps.

(i) Suppose that for a given initial placement of acceptors, a closest to the origin acceptor appears at distance l. Thus a notional spherical volume V_l of radius l, centered at the origin, is initially completely devoid of acceptors.

(ii) Performing averaging over donor's trajectories $\{\mathbf{r}(t)\}$, we consider only such trajectories which never leave V_l up to time moment t. Since $Q[\mathbf{r}(t);t]$ in Eq. (11) is always positive definite for any particular realization $\mathbf{r}(t)$, such a constraint naturally leads to a lower bound on $P(t)$, i.e.,

$$E_0^D\{\exp[-n_A Q[\mathbf{r}(t);t]]\} \geqslant E^D_{0,\mathbf{r}(t)\in V_l}\{\exp[-n_A Q[\mathbf{r}(t);t]]\}, \quad (20)$$

where $E^D_{0,\mathbf{r}(t)\in V_l}\{\cdots\}$ denotes averaging over a subset of all possible donor's trajectories such that they do not leave V_l during time t.

(iii) Considering the term responsible for long-range transfer, $Q[\mathbf{r}(t);t]$, we suppose that the donor is always located on the surface of V_l at the position *closest* to the instantaneous position of the acceptor. Since $W(\rho)$ is a strictly decreasing function of ρ, for any $r(t)\in V_l$, one has $W[|\mathbf{R}(t)|-l] \geqslant W[|\mathbf{r}(t)-\mathbf{R}(t)|]$ and hence $Q[\mathbf{r}(t);t]$ can be majorized by

$$Q[\mathbf{r}(t);t] \leqslant Q(l;t) = \int d\mathbf{R}(0) \times E^A_{\mathbf{R}(0)}\left\{1-\exp\left[-\int_0^t dt' W[|\mathbf{R}(t')|-l]\right]\right\}. \quad (21)$$

Note now that the right-hand-side of the inequality in Eq. (21) is *independent* of the donor's trajectories.

Consequently, collecting (i)–(iii), we arrive at the following *lower* bound on the global decay function:

$$P(t) \geqslant P_{\text{void}}(l) E^D_{0,\mathbf{r}(t)\in V_l}\{1\}\exp[-n_A R(l;t)]. \quad (22)$$

In this equation $P_{void}(l)$ is the probability of having an acceptor-free spherical void of radius l. For random initial placement of acceptors, one has

$$P_{\text{void}}(l) \sim \exp[-n_A V_d l^d]. \quad (23)$$

Further on, in Eq. (22) the symbol $E^D_{0,\mathbf{r}(t)\in V_l}\{1\}$ denotes the measure of such donor's trajectories, which commence at the origin and never leave V_l during time t; at sufficiently large times, $E^D_{0,\mathbf{r}(t)\in V_l}\{1\}$ is given by

$$E^D_{0,\mathbf{r}(t)\in V_l}\{1\} \sim \exp\left[-z_d^2\frac{D_D t}{l^2}\right], \quad (24)$$

z_d being the first zero of the Bessel function $J_{(d-2)/2}(x)$.

Combining the expressions in Eqs. (23) and (24), and assuming spherical symmetry, we finally obtain

$$P(t) \geqslant P_l(t) = \exp\left[-n_A V_d l^d - z_d^2\frac{D_D t}{l^2} - n_A\int_0^t dt' k_l(t')\right]. \quad (25)$$

In the latter equation,

$$k_l(t) = dV_d\int_{l+a}^{\infty} r^{d-1}W(r-l)\tilde{G}_t(r)dr, \quad (26)$$

while $\tilde{G}_t(r)$ is the solution of

$$\frac{\partial \tilde{G}_t(r)}{\partial t} = D_A\left(\frac{\partial^2 \tilde{G}_t(r)}{\partial r^2} + \frac{d-1}{r}\frac{\partial \tilde{G}_t(r)}{\partial r}\right) - W(r-l)\tilde{G}_t(r),$$

$$\tilde{G}_{t=0}(r) = 1; \quad \tilde{G}_t(r\to\infty) = 1, \quad (27)$$

subject, in virtue of condition (iii), to a reflection boundary condition imposed at $r=l+a$:

$$\left.\frac{\partial \tilde{G}_t(r)}{\partial r}\right|_{r=l+a} = 0. \quad (28)$$

Equations (25)–(28) define a family of lower bounds on the global decay function in systems with diffusive donor and acceptors, dependent on the radius l of the notional volume V_l encircling the donor and devoid of acceptors.

To get the optimal lower bound, we will have, in the usual fashion, to maximize the result with respect to l. Below we consider lower and upper bounds on the global decay function in one-dimensional systems with long-range transfer [Eqs. (1) and (2)] between diffusive donor and diffusive acceptors. Corresponding results for two- and three-dimensional systems will be presented elsewhere [24].

V. ONE-DIMENSIONAL SYSTEMS: EXCHANGE-MEDIATED TRANSFER

A. Upper bound

Consider first the derivation of *an upper bound* in one-dimensional systems with a transfer mediated by exchange. Here, Laplace-transformed with respect to time variable t, the solution of Eqs. (27) and (28) reads

$$G_\lambda(r) = \int_0^\infty dt\exp[-\lambda t]G_t(r) = C_1 I_\chi(x) + C_2 K_\chi(x) + \frac{\chi\Gamma\left(1-\frac{\chi}{2}\right)}{\lambda}\left(\frac{x}{2}\right)^{\chi/2}\int_0^1 I_{-\chi/2}(x\xi) \times \xi^{1+\chi/2}(1-\xi^2)^{\chi/2-1}d\xi, \quad (29)$$

where $K_\chi(x)$ and $I_\chi(x)$ are modified Bessel functions, the integral term in the second line is a particular solution (Lommel function), and

$$x = \omega \exp\left(-\gamma\frac{r}{2}\right), \quad x_0 = \omega \exp\left(-\gamma\frac{a}{2}\right),$$

$$\omega = \frac{2}{\gamma}\sqrt{\frac{\alpha_e}{D_A}}, \quad \text{and } \chi = \frac{2}{\gamma}\sqrt{\frac{\lambda}{D_A}}. \tag{30}$$

Now, note that as $r\to\infty$, $x\to 0$, $I_\chi(x)\to 0$, the last term on the right-hand side of Eq. (29) tends to $1/\lambda$, while $K_\chi(x)$ diverges. Hence we set $C_2=0$. Further, we get that the reflective boundary condition at the closest approach distance is fulfilled when

$$C_1 = -\frac{2\chi\Gamma\left(1-\frac{\chi}{2}\right)}{\lambda[I_{\chi-1}(x_0)+I_{\chi+1}(x_0)]}\left(\frac{x_0}{2}\right)^{\chi/2}\int_0^1 I_{1-\chi/2}(x_0\xi) \times \xi^{2+\chi/2}(1-\xi^2)^{\chi/2-1}d\xi. \tag{31}$$

Plugging Eqs. (29) and (31) into Eq. (18) and performing integration, we find that the Laplace-transformed reaction constant $k_u(\lambda)$ is given by

$$k_u(\lambda) = \frac{D_A\gamma x_0^2}{\lambda}\left[{}_2F_3\left(1,1;2,1-\frac{\chi}{2},1+\frac{\chi}{2},\frac{x_0^2}{4}\right) - \frac{2}{\left(1+\frac{\chi}{2}\right)\left(1-\frac{\chi^2}{4}\right)\Gamma(1+\chi)} \times \left(\frac{x_0}{2}\right)^{1+\chi}\frac{{}_1F_2\left(2;2-\frac{\chi}{2},2+\frac{\chi}{2};\frac{x_0^2}{4}\right){}_1F_2\left(1+\frac{\chi}{2};2+\frac{\chi}{2},1+\chi;\frac{x_0^2}{4}\right)}{I_{\chi-1}(x_0)+I_{\chi+1}(x_0)}\right], \tag{32}$$

where ${}_pF_q$ denotes generalized hypergeometric functions.

Leading small-λ (large-t) asymptotic behavior of $k_u(\lambda)$ in Eq. (32) follows

$$k_u(\lambda) \sim 2\sqrt{\frac{D_A}{\lambda}}\frac{1}{1+\sqrt{T_e\lambda}}, \tag{33}$$

where

$$T_e = \left(\frac{K_1(x_0)+[1/2-C+\ln(2/x_0)]I_1(x_0)}{I_1(x_0)}\right)^2\frac{4}{\gamma^2 D_A}, \tag{34}$$

$C\approx 0.577$ being the Euler constant.

This yields, in t-domain, the following asymptotical behavior:

$$\int_0^t dt' k_u(t') = 4\sqrt{\frac{D_A t}{\pi}}\left[1-\sqrt{\frac{\pi T_e}{4t}}+O\left(\frac{1}{t}\right)\right]. \tag{35}$$

Consequently, in 1D systems with transfer mediated by exchange we have the following upper bound on the global decay function:

$$P(t) \leqslant \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}}+2n_A\sqrt{D_A T_e}+O\left(\frac{1}{t^{1/2}}\right)\right]. \tag{36}$$

Before we proceed to the derivation of the lower bound, a few comments are in order.

(a) First of all, we notice that the right-hand side of Eq. (36) coincides with the solution of the so-called target problem—probability that an immobile target survives, in one-dimension, up to time t in the presence of diffusive scavengers which may "destroy" the target upon the first encounter with it [29]. Therefore, in one dimension, at sufficiently long times the kinetic behavior of long-range transfer proceeds exactly in the same way as for contact diffusion-limited target annihilation reaction, despite the fact that here the boundary condition imposed on the donor's surface is reflective and the deactivation of the donor happens, at rate $\alpha_e\exp(-\gamma r)$, at any donor-acceptor distance r.

(b) Parameter T_e in Eq. (34) is the crossover time to the asymptotic stage $\ln P_u(t)\sim -t^{1/2}$ for exchange-mediated transfer in one-dimensional systems with immobile donor and mobile acceptors. Note that $\gamma^2 D_A T_e$ is a nonmonotonic function of x_0. It is large $\sim 1/x_0^4$ when $x_0\ll 1$ (i.e., when D_A is large), such that $T_e\sim\gamma^2 D_A/\alpha_e^2$. In this case, one would first observe, for $0<t<T_e$, an intermediate asymptotical behavior $\ln P(t)\sim -\gamma\alpha t$, which will then cross to the asymptotical behavior in Eq. (36). Next, note that $\gamma^2 D_A T_e$ is also large when $x_0\gg 1$, which happens when D_A is small. Here, $T_e\approx\ln^2(x_0/2)/\gamma^2 D_A$, i.e., T_e is proportional to the first inverse power of D_A (with logarithmic corrections). In this case, the asymptotic decay in Eq. (36) succeeds the static quenching decay in Eq. (4), which is valid in progressively larger time domain the closer D_A is to zero.

(c) Finally, we remark that despite the fact that the result in Eq. (35) is independent of both α_e and γ, which are the

only parameters characterizing the transfer rate and thus "represent" reaction, it does not mean that it can be simply obtained by expanding $G(r)=\Sigma_{n=0}^{\infty}\alpha_e^n G_n(r)$ and considering the zeroth term only. In general, Eq. (35) is essentially a nonperturbative result and cannot be obtained using a perturbative expansion of $G_t(r)$ in powers of α_e, unless, of course, one manages to sum the whole series. On the other hand, Eq. (35) can be straightforwardly derived approximating the transfer rate by a step function ("square well" approximation).

Indeed, suppose that $\gamma a<1$ and consider separately the solution of Eqs. (27) and (28) for $a\leqslant r\leqslant 1/\gamma$ and $r\geqslant 1/\gamma$. In the first interval we approximate $\exp[-\gamma r]$ by $\exp[-\gamma a]$, and find that the Laplace-transformed solution of the Schrödinger equation which obeys the reflecting boundary condition reads

$$G_\lambda^{(1)}=\frac{1}{\lambda+\alpha_e\exp[-\gamma a]}+C_1\cosh\left[\sqrt{\frac{\lambda+\alpha_e\exp[-\gamma a]}{D_A}}(r-a)\right]. \quad (37)$$

On the other hand, in the domain $r\geqslant 1/\gamma$, the transfer term can be neglected, and we have

$$G_\lambda^{(2)}(r)=\frac{1}{\lambda}+C_2\exp\left[-\sqrt{\frac{\lambda}{D_A}}\left(r-\frac{1}{\gamma}\right)\right]. \quad (38)$$

Since $G_\lambda(r)$ and its first derivative have to be continuous functions at $r=1/\gamma$, we have two complementary equations which define the coefficients C_1 and C_2. Determining these coefficients, we find that the leading small-λ behavior of $k_u(\lambda)$ follows

$$k_u(\lambda)=2\alpha_e\exp[-\gamma a]\int_a^{1/\gamma}G_\lambda^{(1)}(r)dr=2\sqrt{\frac{D_A}{\lambda}}\frac{1}{1+\sqrt{T_e'\lambda}}, \quad (39)$$

where

$$T_e'=\frac{\exp[a\gamma]}{\alpha_e}\coth^2\left(\frac{x_0}{2}\right). \quad (40)$$

Note that $k_u(\lambda)$ in Eq. (39) has exactly the same form as $k_u(\lambda)$ in Eq. (33), which means that the "square well" approximation captures well the leading behavior of the effective reaction rate. The crossover time T_e' has a different form compared to the exact one, Eq. (34); it exhibits, however, quite a "correct" behavior in the case $x_0\ll 1$ (fast diffusion) when $T_e'\sim\gamma^2 D_A/\alpha_e^2$.

B. Lower bound

Consider now a lower bound on $P(t)$ for one-dimensional systems with transfer mediated by exchange interactions. The Laplace-transformed solution of Eqs. (27) and (28) reads

$$\tilde{G}_\lambda(r)=C_1 I_\chi(xe^{\gamma l/2})+\frac{\chi\Gamma(1-\chi/2)}{\lambda}\left(\frac{xe^{\gamma l/2}}{2}\right)^{\chi/2}\int_0^1 I_{-\chi/2}(x\xi e^{\gamma l/2})\times\xi^{1+\chi/2}(1-\xi^2)^{\chi/2-1}d\xi, \quad (41)$$

where C_1 is given by Eq. (31). Plugging the expression in Eq. (41) into Eq. (26) and performing integration, we find that $k_l(\lambda)$ obeys

$$k_l(\lambda)\equiv k_u(\lambda), \quad (42)$$

where $k_u(\lambda)$ is determined by Eq. (32). Consequently, the lower bound on $P(t)$, Eq. (25), at sufficiently long times attains the following form:

$$P_l(t)\sim\exp\left[-2n_A l-\pi^2\frac{D_D t}{l^2}-4n_A\sqrt{\frac{D_A t}{\pi}}\right]. \quad (43)$$

As we have already mentioned, the result in Eq. (43) represents rather a family of lower bounds dependent on parameter l—radius of a notional volume initially devoid of acceptors. The "best" lower bound thus would be the highest one. Optimizing Eq. (43) with respect to l, we find that the highest lower bound is achieved when $l=(\pi^2 D_D t/n_A)^{1/3}$, and is given by

$$P_{l,max}(t)\sim\exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}}-3n_A^{2/3}(\pi^2 D_D t)^{1/3}\right]. \quad (44)$$

On comparing the asymptotic behavior predicted by the maximal lower bound in Eq. (44) against the upper bound in Eq. (36) we notice that both bounds converge asymptotically to give an exact result in Eq. (7).

VI. ONE-DIMENSIONAL SYSTEMS: MULTIPOLAR TRANSFER

A. Upper bound

Consider now, within the "square well" approximation, an upper bound in the case of multipolar transfer in Eq. (1). Approximating the actual transfer rate $W(r)$ in Eq. (1) by a step function

$$W(r)=\begin{cases}\alpha_m(r_0/a)^n, & a\leqslant r\leqslant r_0,\\ 0, & r\geqslant r_0,\end{cases}$$

we find that in the interval $a\leqslant r\leqslant r_0$ the Laplace-transformed solution of Eq. (19) obeys

$$G_\lambda^{(1)}=\frac{1}{\lambda+\alpha_m(r_0/a)^n}+C_1\cosh\left[\sqrt{\frac{\lambda+\alpha_m(r_0/a)^n}{D_A}}(r-a)\right], \quad (45)$$

while in the domain $r\geqslant r_0$ it follows

$$G_\lambda^{(2)}(r)=\frac{1}{\lambda}+C_2\exp\left[-\sqrt{\frac{\lambda}{D_A}}(r-r_0)\right]. \quad (46)$$

Constants C_1 and C_2 are to be chosen in such a way that both $G_\lambda(r)$ and its first derivative are continuous functions at $r=r_0$.

Determining these constants, plugging Eq. (46) into Eq. (18) and performing integration, we find that the Laplace-transformed $k_u(t)$ is given by

$$k_u(\lambda) = 2\sqrt{\frac{D_A}{\lambda}}\left[1+\sqrt{\frac{\lambda a^n}{\alpha_m r_0^n}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0-a)\right)\right]^{-1} + \frac{2\alpha_m (r_0/a)^n (r_0-a)}{\lambda+\alpha_m (r_0/a)^n}. \tag{47}$$

This yields, in t domain,

$$\int_0^t k_u(t')dt' = 4\sqrt{\frac{D_A t}{\pi}}\left[1-\sqrt{\frac{\pi a^n}{4\alpha_m r_0^n t}} \times\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0-a)\right)+O\left(\frac{1}{t}\right)\right]. \tag{48}$$

Consequently, the global decay function $P(t)$ in one-dimensional systems with diffusive donor and acceptors interacting via multipolar transfer rate in Eq. (1) is bounded from above by

$$P(t) \leqslant \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}}+2n_A\sqrt{\frac{D_A a^n}{\alpha_m r_0^n}} \times\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0-a)\right)\right]. \tag{49}$$

B. Lower bound

Turning next to evaluation of the lower bound on $P(t)$ we introduce parameter $\delta > a$, and approximate the actual transfer rate by a step function of the form

$$W(r) = \begin{cases} \alpha_m (r_0/a)^n, & l+a \leqslant r \leqslant l+\delta, \\ 0, & r \geqslant \delta. \end{cases}$$

The approximate solution of Eqs. (27) in the interval $l+a \leqslant r \leqslant l+\delta$ has the form

$$\tilde{G}_\lambda^{(1)} = \frac{1}{\lambda+\alpha_m (r_0/a)^n} + C_1 \cosh\left[\sqrt{\frac{\lambda+\alpha_m (r_0/a)^n}{D_A}}(r-l-a)\right], \tag{50}$$

while in the domain $r \geqslant l+\delta$ it is given by

$$\tilde{G}_\lambda^{(2)}(r) = \frac{1}{\lambda} + C_2 \exp\left[-\sqrt{\frac{\lambda}{D_A}}(r-l-\delta)\right]. \tag{51}$$

Again, requiring continuity of $\tilde{G}_\lambda(r)$ and of its first derivative at $r=l+\delta$, we determine C_1 and C_2, which yields, after straightforward calculations, the following expression:

$$k_l(\lambda) = 2\sqrt{\frac{D_A}{\lambda}}\left[1+\sqrt{\frac{\lambda a^n}{\alpha_m r_0^n}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(\delta-a)\right)\right]^{-1} + \frac{2\alpha_m (r_0/a)^n (\delta-a)}{\lambda+\alpha_m (r_0/a)^n}. \tag{52}$$

We find then that in the t domain, the leading behavior of $\int_0^t k_l(t')dt'$ is given by

$$\int_0^t k_l(t')dt' = 4\sqrt{\frac{D_A t}{\pi}} - 2\sqrt{\frac{D_A a^n}{\alpha_m r_0^n}} \times\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(\delta-a)\right)+O\left(\frac{1}{t^{1/2}}\right). \tag{53}$$

Consequently, an optimized lower bound on $P(t)$ reads

$$P(t) \geqslant \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}} - 3n_A^{2/3}(\pi^2 D_D t)^{1/3} + 2n_A\sqrt{\frac{D_A a^n}{\alpha_m r_0^n}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(\delta-a)\right)\right]. \tag{54}$$

On comparing the results in Eqs. (49) and (54), we notice that again both bounds converge as $t \to \infty$ determining exact asymptotic decay of the excited donor, Eq. (7).

VII. CONCLUSIONS

To conclude, we have studied analytically direct energy transfer between diffusive excited donor and diffusive unexcited acceptors mediated by multipolar or exchange interactions. Extending a nonperturbative approach by Bray and Blythe [21] (originally developed for contact diffusion-controlled reactions) over the case of long-range transfer, we have determined exactly long-time asymptotics of the donor decay function in one-dimensional systems. We have shown that the leading long-time behavior is independent of the diffusion constant D_D of the donor molecule, and has exactly the same form as that describing the contact process. This finding is in apparent contradiction with the results in Eqs. (5) and (6).

We proceed to show elsewhere [24] that also in two-dimensional systems the leading long-time behavior will be independent of D_D, while in 3D a similar approach will give rise to a fluctuation-induced lower bound on the decay function which, in some range of parameters, is better (higher) than predictions based on the standard Smoluchowski approach.

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