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Diffusion-Influenced Excited-State Reversible Geminate ABCD Reaction in the Presence of an External Field

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: We obtained the exact Green functions, in the Laplace domain, for a diffusion-influenced excited-state reversible geminate ABCD reaction with two different lifetimes and quenching processes under a constant external field in one dimension. Analytic expressions for the survival probabilities of the initial and final states are obtained in the time domain at short and long times, respectively. The short-time approximations obtained in this work are valid for $t < |K|^{-1}$, where K depends on several parameters of the system. The analysis of the long-time asymptotic behaviors reveals rather complex kinetic transitions dependent upon the field and lifetimes. We also find a destructive interplay leading to the reduction in the number of kinetic transitions similar to that found for the excited-state geminate ABC reaction with an external field in one dimension.

Keywords: diffusion-influenced · Green function · external field · geminate reaction · kinetics

Introduction

Under most experimental conditions, an external field is inevitable, be it gravitational, electric, or magnetic (strictly speaking, all of them exist at all times, usually with weak strengths). Such an external field may increase or decrease the population of a specific state of a pair (e.g., magnetic field-dependent population of the singlet state of a radical ion pair)[1] or the rate of reaction (e.g., the rate of reaction between charged particles under an electric field).[2] Therefore, the reaction kinetics may show field-dependent behavior (field effect). In the present model, we assume a constant (external) electric field, which can be easily realized in usual conditions and its effect can be interpreted relatively in a straightforward manner compared to that of the magnetic field effect (involving spin dynamics).[3]

The effect of the constant electric field on the diffusion-influenced reaction has been studied for several decades. It has been shown as a kinetic transition behavior in the trapping problem (chemical species in excess are static and the other species are moving) where the long-time asymptotic behavior changes from a stretched exponential relationship, $\exp(-t^{\alpha})$, to a purely exponential one by increasing the strength of an applied external field.[4] For the target problem (the opposite case to the trapping problem), Tachiya et al. have studied the field-dependent steady-state rate coefficient.[2] For geminate reactions, the field effect causes a kinetic transition behavior from a power-law relationship to an exponential one, as the field strength increases.[5–8]

A geminate reaction is interesting because the system can be readily prepared by laser pulses and its theoretical study does not involve the many-body effects. Examples of geminate reactions are the excited-state proton transfer from a photoacid to solvent (PTTS),[9] fluorescence kinetics in Green Fluorescence Protein,[10] and so forth. For many cases, the exact Green functions for the geminate problems have been obtained in the Laplace or time domain.[5–8,11–13] These Green functions have been utilized in the accurate Brownian dynamics simulations[14] and in the theories for the corresponding many-body problems.[15] Thus, the study of the field effect on the geminate reaction may provide some insights into the many-body problems.

Hong and Noolandi were able to obtain the exact Green function for an irreversible geminate recombination (or neutralization of charged particles) under the Coulomb potential in the presence of an external electric field in three dimensions (3D). The analysis of the long-time asymptotic behavior revealed a kinetic transition behavior arising from

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the field effect, whose dynamics change from a power-law to an exponential relationship as the field strength increases.[5]

For the reversible geminate A+B↔C (ABC) reactions in one dimension (1D), Kim et al. investigated the field effect on these reactions by mapping the exact Green functions for the excited-state reversible geminate ABC (geminate ES-ABC) reaction without a field[11] into those for the reversible geminate ground-state ABC (geminate GS-ABC) and geminate ES-ABC reactions under a constant external field.[6,7] They found that the number of kinetic transitions may vary, which is caused by the interplay of the field and lifetimes.[7]

In our previous work for the ground-state reversible geminate A+B↔C+D (ABCD) reaction,[12] we obtained the exact Green functions in the Laplace domain and investigated the field effect on the survival probabilities of the reactant and product states. By analyzing the long-time asymptotic behavior, we found rather complex kinetic transition behavior depending on the directions of the applied fields and the difference of the field strengths on the reactant and product states. By analogy to the geminate ES-ABC reaction, for the excited-state reversible geminate ABCD (geminate ES-ABCD) reaction under an external field, it is expected that the number of kinetic transition may also vary by a similar destructive interplay. Therefore, we expect an even more complex field-dependent kinetic transition behavior than that for the ground-state reversible geminate ABCD reaction.

In this work, we investigate the geminate ES-ABCD reaction with two different lifetimes and an added quenching process under the influence of a constant external field by analyzing the survival probabilities obtained from the exact Green functions in the Laplace domain.

Exact Results in Laplace Space

The schematic representation of the ES-ABCD reaction in the present work is given by [Eq. (1a)]–[Eq. (1e)]

$$A^* + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C^* + D \tag{1a}$$

$$A^* + B \xrightarrow{k_{q1}} A + B \tag{1b}$$

$$C^* + D \xrightarrow{k_{q2}} C + D \tag{1c}$$

$$A^* \xrightarrow{k_{u1}} A \tag{1d}$$

$$C^* \xrightarrow{k_{u2}} C \tag{1e}$$

The superscript * denotes the excited state, whereas k_1 and k_2 are the forward and backward rate coefficients, respectively. k_{ui} ($i=1$ and 2) is the unimolecular decay rate coefficient and k_{qi} ($i=1$ and 2) is the quenching rate coefficient, which is introduced in order to describe the collision induced deactivation of a reactive molecule with its reaction partner.

In the present system, there are two different states to be considered. Let us denote state 1 for A^* and B particles, and state 2 for C^* and D particles. Then, the distance between A^* and B (C^* and D) is denoted by x_1 (x_2), which ranges from 0 to infinity. The relative diffusion constants in these states, which may differ, are $D_1 = D_{A^*} + D_B$ for state 1 and $D_2 = D_{C^*} + D_D$ for state 2. The linear potentials for states 1 and 2 are $u(x_1)/k_BT = 2a_1x_1$ and $u(x_2)/k_BT = 2a_2x_2$, respectively. Note that, when $a_i > 0$, the particles for the corresponding state move towards each other whereas they move away when $a_i < 0$. The diffusion operators in these states are determined by [Eq. (2)]

$$\Lambda_i \equiv D_i \frac{\partial}{\partial x_i} e^{-2a_ix_i} \frac{\partial}{\partial x_i} e^{2a_ix_i} \tag{2}$$

and these describe the relative motion of an A^*B pair for $i=1$ and a C^*D pair for $i=2$.

Let us denote the probability of finding an A^*B pair separated by x_1 at time t by $p_1(x_1,t)$ and, similarly, $p_2(x_2,t)$ for a C^*D pair. These probability densities obeys the following Smoluchowski-type reaction-diffusion equations [Eq. (3a)] and [Eq. (3b)]:

$$\frac{\partial}{\partial t} p_1(x_1,t) = \Lambda_1 p_1(x_1,t) - [W_1(x_1) + W_{q1}(x_1) + k_{u1}] p_1(x_1,t) + W_2(x_1) p_2(0,t) \ , \tag{3a}$$

$$\frac{\partial}{\partial t} p_2(x_2,t) = \Lambda_2 p_2(x_2,t) - [W_2(x_2) + W_{q2}(x_2) + k_{u2}] p_2(x_2,t) + W_1(x_2) p_1(0,t) \ , \tag{3b}$$

where the sink terms which describe the reactions are defined as [Eq. (4)]

$$W_i(x_j) \equiv k_i\delta(x_j),\ W_{qi}(x_i) \equiv k_{qi}\delta(x_i) \tag{4}$$

The delta functions in the sink terms imply that the reactions can occur only at the contact distance (or at the origin) of each state. Because the reaction is introduced using these sink terms, we assume that the p_i obeys the reflecting boundary conditions at the origin of each state, $(\partial/\partial x_i + 2a_i) p_i(x_i,t)|_{x_i=0} = 0$, i.e., $\int_0^\infty dx_i\, \Lambda_i p_i(x_i,t) = 0$.

Let us consider an initial state 1, with A^* and B separated by a distance x_0, ([Eq. (5)])

$$p_1(x_1,0) = \delta(x_1 - x_0),\ p_2(x_2,0) = 0 \tag{5}$$

The probability density ("reactive Green function"), obeying these initial conditions [Eq. (5)], of finding an A^*B pair separated by a distance x_1 at time t is denoted by $p_1(x_1,t|x_0)$, and similarly, $p_2(x_2,t|x_0)$ for a C^*D pair.

In the Laplace domain $[\hat{f}(s) = \int_0^\infty dt\, f(t) \exp(-st)]$, the evolution equations of the reactive Green functions (GFs) for the chosen initial condition are expressed as [Eq. (6a)] and [Eq. (6b)]

$$s\hat{p}_1(x_1,s|x_0) = \delta(x_1-x_0) + \Lambda_1\hat{p}_1(x_1,s|x_0) - [W_1(x_1)+W_{q1}(x_1)+k_{u1}]\hat{p}_1(x_1,s|x_0) + W_2(x_1)\hat{p}_2(0,s|x_0) \quad (6a)$$

$$s\hat{p}_2(x_2,s|x_0) = \Lambda_2\hat{p}_2(x_2,s|x_0) - [W_2(x_2)+W_{q2}(x_2)+k_{u2}]\hat{p}_2(x_2,s|x_0) + W_1(x_2)\hat{p}_1(0,s|x_0) \quad (6b)$$

By substituting [Eq. (4)], [Eq. (6a)] and [Eq. (6b)] can be rewritten as [Eq. (7a)] and [Eq. (7b)]

$$(s_{u1}-\Lambda_1)\hat{p}_1(x_1,s|x_0) = \delta(x_1-x_0) - [k_1'\hat{p}_1(0,s|x_0) - k_2\hat{p}_2(0,s|x_0)]\delta(x_1), \quad (7a)$$

$$(s_{u2}-\Lambda_2)\hat{p}_2(x_2,s|x_0) = [k_1\hat{p}_1(0,s|x_0) - k_2'\hat{p}_2(0,s|x_0)]\delta(x_2), \quad (7b)$$

where $s_{ui} = s + k_{ui}$ and $k_i' = k_i + k_{qi}$.

By introducing the non-reactive Green function (GF), $\hat{G}_i(x_i,s|x_0)$, which satisfies [Eq. (8)]

$$(s-\Lambda_i)\hat{G}_i(x_i,s|x_0) = \delta(x_i-x_0), \quad (8)$$

with the reflecting boundary condition, $(\partial/\partial x_i + 2a_i)\hat{G}_i(x_i,s|x_0)|_{x_i=0} = 0$, [Eq. (7a)] and [Eq. (7b)] can be rewritten as [Eq. (9a)] and [Eq. (9b)]

$$\hat{p}_1(x_1,s|x_0) = \hat{G}_1(x_1,s_{u1}|x_0) - [k_1'\hat{p}_1(0,s|x_0) - k_2\hat{p}_2(0,s|x_0)]\hat{G}_1(x_1,s_{u1}|0), \quad (9a)$$

$$\hat{p}_2(x_2,s|x_0) = [k_1\hat{p}_1(0,s|x_0) - k_2'\hat{p}_2(0,s|x_0)]\hat{G}_2(x_2,s_{u2}|0). \quad (9b)$$

Setting $x_i = 0$ in [Eq. (9a)] and [Eq. (9b)], one gets [Eq. (10a)] and [Eq. (10b)]

$$\hat{p}_1(0,s|x_0) = \frac{1+k_2'\hat{g}_2(s_{u2})}{\hat{h}(s)}\hat{G}_1(0,s_{u1}|x_0), \quad (10a)$$

$$\hat{p}_2(0,s|x_0) = \frac{k_1\hat{g}_2(s_{u2})}{\hat{h}(s)}\hat{G}_1(0,s_{u1}|x_0), \quad (10b)$$

where $\hat{g}_i(s) = \hat{G}_i(0,s|0)$ and [Eq. (11)]

$$\hat{h}(s) = 1 + k_1'\hat{g}_1(s_{u1}) + k_2'\hat{g}_2(s_{u2}) + (k_1'k_2' - k_1k_2)\hat{g}_1(s_{u1})\hat{g}_2(s_{u2}). \quad (11)$$

Substituting [Eq. (10a)] and [Eq. (10b)] into [Eq. (9a)] and [Eq. (9b)], one can obtain the reactive GFs in terms of the non-reactive GFs as [Eq. (12a)] and [Eq. (12b)]

$$\hat{p}_1(x_1,s|x_0) = \hat{G}_1(x_1,s_{u1}|x_0) - \frac{k_1' + (k_1'k_2' - k_1k_2)\hat{g}_2(s_{u2})}{\hat{h}(s)} \times \hat{G}_1(x_1,s_{u1}|0)\hat{G}_1(0,s_{u1}|x_0), \quad (12a)$$

$$\hat{p}_2(x_2,s|x_0) = \frac{k_1}{\hat{h}(s)}\hat{G}_2(x_2,s_{u2}|0)\hat{G}_1(0,s_{u1}|x_0), \quad (12b)$$

By setting $k_{ui} = 0$ and $k_{qi} = 0$, [Eq. (12a)] and [Eq. (12b)] reduces to results for the ground-state reversible geminate ABCD reaction with the applied field, see [Eq. (21a)] and [Eq. (21b)] in Ref. [8]. One gets the solution for the geminate ES-ABCD reaction by setting $a_i = 0$ in [Eq. (12a)] and [Eq. (12b)].[12] The solution for the geminate ES-ABC reaction in the presence of a constant external field is obtained from [Eq. (12a)] and [Eq. (12b)] by setting $a_2 = 0$, $k_{q2} = 0$, and by replacing $\hat{g}_2(s_{u2})$ and $\hat{G}_2(x_2,s_{u2}|x_0)$ by $1/s_{u2}$. It is obvious because the C^* state can be changed only by the unimolecular decay in the absence of a D particle. In this case, x_2 is replaced by * representing the bound state and $\hat{p}_2(x_2,s|x_0)$ becomes the binding probability $\hat{p}_2(*,s|x_0)$.

The survival probabilities for states 1 and 2, $S_i(t|x_0)$, are defined as the integrals of the corresponding probability densities, [Eq. (13)]

$$S_i(t|x_0) = \int_0^\infty dx_i\, p_i(x_i,t|x_0). \quad (13)$$

Because $\int_0^\infty dx_i\, \hat{G}_i(x_i,s|x_0) = s^{-1}$, by the integration of [Eq. (12a)] and [Eq. (12b)], one gets [Eq. (14a)] and [Eq. (14b)]

$$\hat{S}_1(s|x_0) = \frac{1}{s_{u1}}\left[1 - \frac{k_1' + (k_1'k_2' - k_1k_2)\hat{g}_2(s_{u2})}{\hat{h}(s)}\hat{G}_1(0,s_{u1}|x_0)\right], \quad (14a)$$

$$\hat{S}_2(s|x_0) = \frac{k_1}{s_{u2}\hat{h}(s)}\hat{G}_1(0,s_{u1}|x_0). \quad (14b)$$

The normalization condition [Eq. (15)],

$$s_{u1}\hat{S}_1(s|x_0) + s_{u2}\hat{S}_2(s|x_0) + k_{q1}\hat{p}_1(0,s|x_0) + k_{q2}\hat{p}_2(0,s|x_0) = 1, \quad (15)$$

can be easily verified.

In the previous work,[8] we have obtained the non-reactive GF, $\hat{G}_i(x_i,s|x_0)$, in the presence of an external field. Introducing the transformation, $F_i(x,t|x_0) = \exp[a_i(x - x_0 + a_iD_it)]G_i(x,t|x_0)$, in the Laplace domain, we have [Eq. (16a)]–[Eq. (16c)]

$$\hat{F}_i(x,s|x_0) = \frac{\exp[-\sqrt{s/D_i}|x-x_0|]}{2\sqrt{D_is}} + \frac{(\sqrt{s}+a_i\sqrt{D_i})\exp[-\sqrt{s/D_i}(x+x_0)]}{2\sqrt{D_is}(\sqrt{s}-a_i\sqrt{D_i})}, \quad (16a)$$

$$\hat{F}_i(x,s|0)=\hat{F}_i(0,s|x)=\frac{\exp[-\sqrt{s/D_i}x]}{\sqrt{D_i s}-D_i a_i}, \quad (16b)$$

$$\hat{f}_i(s)=\hat{F}_i(0,s|0)=\left(\sqrt{D_i s}-D_i a_i\right)^{-1}. \quad (16c)$$

Note that $\hat{G}_i(x,s|x_0)=\exp[-a_i(x-x_0)]\hat{F}_i(x,s+a_i^2D_i|x_0)$ in the Laplace domain.

Inserting [Eq. (16c)] into [Eq. (11)], we get [Eq. (17)]

$$h(s)=\frac{(\sqrt{s_1}+\alpha''_1)(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2}{(\sqrt{s_1}-a_1\sqrt{D_1})(\sqrt{s_2}-a_2\sqrt{D_2})}, \quad (17)$$

where we have defined $s_i=s_{ui}+a_i^2D_i$, $\alpha_i=k_i/\sqrt{D_i}$, $\alpha'_i=(k_i+k_{qi})/\sqrt{D_i}$, and $\alpha''_i=\alpha'_i-a_i\sqrt{D_i}$.

Substituting [Eq. (16a)]–[Eq. (16c)] and [Eq. (17)] into [Eq. (12a)] and [Eq. (12b)] and after some manipulation, one obtains the GFs [Eq. (18a)] and [Eq. (18b)]:

$$e^{a_1(x_1-x_0)}\hat{p}_1(x_1,s|x_0)=\hat{F}_1(x_1,s_1|x_0)-\frac{\alpha'_1(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2}{(\sqrt{s_1}+\alpha''_1)(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2}\times\frac{\exp[-\sqrt{s_1/D_1}(x_1+x_0)]}{\sqrt{D_1}(\sqrt{s_1}-a_1\sqrt{D_1})}, \quad (18a)$$

$$e^{a_2x_2-a_1x_0}\hat{p}_2(x_2,s|x_0)=\frac{\alpha_1\exp[-\sqrt{s_2/D_2}x_2-\sqrt{s_1/D_1}x_0]}{\sqrt{D_2}[(\sqrt{s_1}+\alpha''_1)(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2]}. \quad (18b)$$

Generally, [Eq. (18a)] and [Eq. (18b)] cannot be inverted analytically, except the special case when $K=0$ where ([Eq. (19)])

$$K\equiv(k_{u2}+a_2^2D_2)-(k_{u1}+a_1^2D_1), \quad (19)$$

which are given in Appendix A.

The survival probabilities are obtained by inserting [Eq. (16a)]–[Eq. (16c)] and [Eq. (17)] into [Eq. (14a)] and [Eq. (14b)] to obtain as [Eq. (20a)] and [Eq. (20b)]

$$1-s_{u1}\hat{S}_1(s|x_0)=\frac{[\alpha'_1(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2]\exp[(a_1-\sqrt{s_1/D_1})x_0]}{(\sqrt{s_1}+\alpha''_1)(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2}, \quad (20a)$$

$$s_{u2}\hat{S}_2(s|x_0)=\frac{\alpha_1(\sqrt{s_2}-a_2\sqrt{D_2})\exp[(a_1-\sqrt{s_1/D_1})x_0]}{(\sqrt{s_1}+\alpha''_1)(\sqrt{s_2}+\alpha''_2)-\alpha_1\alpha_2}, \quad (20b)$$

Similarly, [Eq. (20a)] and [Eq. (20b)] cannot be inverted analytically except for the case when $K=0$ (see Appendix A).

Short-Time Behavior

For the ABC and GS-ABCD reactions, it is known that the short-time kinetics can be approximated better by using the generalized Smolulchowski theory (GST) for the longer times than a simple exponential decay. Moreover, the entire kinetics of the survival probability can be approximated by the sum of the GST term and its long-time asymptotic term.[15,16] This approximation describes the kinetics over the whole time domain excellently, in which the GST is the leading term.

However, the GST is not satisfactory for the geminate ES-ABCD reaction in the absence of an external field at longer times.[12] For the geminate GS-ABCD reaction in the presence of an external field the GST again does not give satisfactory results and, therefore, we introduced an improved short-time approximation which gives more accurate results over longer times.[8] Now we employ a similar short-time approximation to the present system which is valid for $t<|K|^{-1}$.

Let us start from [Eq. (20a)] and [Eq. 20b)] and introduce the short-time approximation, $s_i\approx s_m=s+m$, where ([Eq. (21)])

$$m=\min\{k_{u1}+a_1^2D_1,k_{u2}+a_2^2D_2\}. \quad (21)$$

Because $\Delta s_i\equiv|\max\{s_i-s_m|i=1,2\}|=|K|$ is negligible compared to s_i at short times ($s_i\gg\Delta s_i$), $s_i\approx s_m$ is a reasonable short-time approximation. As time increases, s decreases and Δs_i becomes comparable to s_i. When $s_m\approx O(\Delta s_i)$, this approximation is no longer valid, that is to say $t<|K|^{-1}$ is the range of validity of this short-time approximation. Substituting s_i with s_m in [Eq. (20a)] and [Eq. (20b)], we obtain [Eq. (22a)] and [Eq. (22b)]

$$\hat{S}_1(s_m-m|x_0)\approx\frac{1}{s_m-K_1}\times\left\{1-\frac{\alpha'_1(\sqrt{s_m}+\alpha''_2)-\alpha_1\alpha_2}{(\sqrt{s_m}+\sigma_1)(\sqrt{s_m}+\sigma_2)}\exp\left[\left(a_1-\sqrt{\frac{s_m}{D_1}}\right)x_0\right]\right\}, \quad (22a)$$

$$\frac{\hat{S}_2(s_m|x_0)}{\alpha_1 e^{a_1x_0}}\approx\frac{(\sqrt{s_m}-a_2\sqrt{D_2})\exp[-\sqrt{s_m/D_1}x_0]}{(s_m-K_2)(\sqrt{s_m}+\sigma_1)(\sqrt{s_m}+\sigma_2)}, \quad (22b)$$

where [Eq. (23)]

$$2\sigma_i=\alpha''_1+\alpha''_2+(-1)^i\sqrt{(\alpha''_1-\alpha''_2)^2+4\alpha_1\alpha_2}. \quad (23)$$

Here, we have defined [Eq. (24)]

$$K_i=m-k_{ui}.\ (i=1,2) \quad (24)$$

The analytic expression in the time domain can be obtained by inverting [Eq. (22a)] and [Eq. (22b)] as [Eq. (25a)] and [Eq. (25b)]

$$\begin{aligned}\frac{S_1(t|x_0)e^{mt}-e^{K_1t}}{e^{a_1x_0}}\approx&\frac{\sigma_1[\alpha_1'(\alpha_2''-\sigma_1)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_1^2-K_1)}W(\chi_0,\sigma_1\sqrt{t})\\&-\frac{\sigma_2[\alpha_1'(\alpha_2''-\sigma_2)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_2^2-K_1)}W(\chi_0,\sigma_2\sqrt{t})\\&-\frac{\alpha_1'(\alpha_2''+\sqrt{K_1})-\alpha_1\alpha_2}{2(\sigma_1-\sqrt{K_1})(\sigma_2-\sqrt{K_1})}W\left(\chi_0,\sqrt{K_1t}\right)\\&-\frac{\alpha_1'(\alpha_2''+\sqrt{K_1})-\alpha_1\alpha_2}{2(\sigma_1+\sqrt{K_1})(\sigma_2+\sqrt{K_1})}W\left(\chi_0,-\sqrt{K_1t}\right),\end{aligned}\tag{25a}$$

$$\begin{aligned}\frac{S_2(t|x_0)e^{mt-a_1x_0}}{\alpha_1}\approx&\frac{\sigma_1(\sigma_1+a_2\sqrt{D_2})}{(\sigma_2-\sigma_1)(\sigma_1^2-K_2)}W(\chi_0,\sigma_1\sqrt{t})\\&-\frac{\sigma_2(\sigma_2+a_2\sqrt{D_2})}{(\sigma_2-\sigma_1)(\sigma_2^2-K_2)}W(\chi_0,\sigma_2\sqrt{t})\\&+\frac{\sqrt{K_2}+a_2\sqrt{D_2}}{2(\sigma_1-\sqrt{K_2})(\sigma_2-\sqrt{K_2})}W\left(\chi_0,\sqrt{K_2t}\right)\\&+\frac{\sqrt{K_2}-a_2\sqrt{D_2}}{2(\sigma_1+\sqrt{K_2})(\sigma_2+\sqrt{K_2})}W\left(\chi_0,-\sqrt{K_2t}\right)\end{aligned}\tag{25b}$$

where $\chi_0=x_0/\sqrt{4D_1t}$, $W(x,y)=\exp(2xy+y^2)\mathrm{erfc}(x+y)$, and $\mathrm{erfc}(x)=1-\mathrm{erf}(x)$ is the complementary error function. When $|K|\ll 1$, [Eq. (25a)] and [Eq. (25b)] can be short-time approximate analytic solutions accurate towards a fairly long time regime. When $K=0$, $s_i=s_m$, and the resulting $S_i(t|x_0)$'s are exact (see [Eq. (A6a)] and [Eq. (A6b)] in Appendix A).

In Figure 1, we demonstrate the short-time approximation to the effective survival probability $S_1(t|x_0)e^{mt}$ in comparison with the exact solution obtained from the numerical inversion of [Eq. (20a)], a) when $a_2>0$ and b) when $a_2<0$. The short-time approximation is valid for $t<0.2|K|^{-1}=20$ ns. It is interesting to note that the time range of validity for the short-time approximation is much longer in each graph for the negative a_1 than that for the positive.

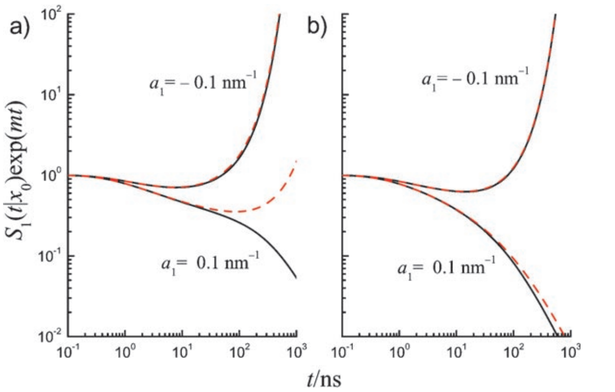

Figure 1. The time-dependence of the effective survival probability, $S_1(t|x_0)e^{mt}$, for positive and negative values of a_1. The solid lines in this Figure and all the other figures are the numerically inverted exact solutions, [Eq. (20a)]. The dashed lines are the short-time approximation calculated from [Eq. (25a)]. The parameter values are $k_1=k_2=1.0$ nm/ns, $k_{q1}=k_{q2}=0.1$ nm/ns, $k_{u1}=k_{u2}=0.1$ ns^{-1}, $D_1=1.0$ nm^2/ns, $D_2=2.0$ nm^2/ns, $x_0=1.0$ nm, and a_1 varies as indicated in the Figure ($K>0$). The value of a_2 is given by a) $a_2=0.1$ nm^{-1} and b) $a_2=-0.1$ nm^{-1}.

Long-Time Asymptotic Behavior

As mentioned earlier in the Exact Results in Laplace Space section, the time-domain expressions of the survival probabilities can not be obtained analytically by inverting [Eq. (20a)] and [Eq. (20b)] in the general case. However, as we have shown in previous work,[8,12] the long-time asymptotic behavior can be analyzed in the time-domain.

We start from the series expansions of [Eq. (20a)] and [Eq. (20b)] for the survival probabilities in the region of $s=-m$, which lead to [Eq. (26a)] and [Eq. (26b)]

$$\hat{S}_1(s_m-m|x_0)=\frac{u_1}{s_m-K_1}+\frac{u_2\sqrt{s_m}}{s_m-K_1}+\sum_{j=0}^{\infty}\varepsilon_j s_m^{j/2},\tag{26a}$$

$$\hat{S}_2(s_m-m|x_0)=\frac{v_1}{s_m-K_2}+\frac{v_2\sqrt{s_m}}{s_m-K_2}+\sum_{j=0}^{\infty}\phi_j s_m^{j/2},\tag{26b}$$

where K_i is defined in [Eq. (24)] and the coefficients u_1, u_2, v_1, v_2, ε_j, and ϕ_j are yet to be determined.

By inverting [Eq. (26a)] and [Eq. (26b)] into the time domain, one can obtain [Eq. (27a)] and [Eq. (27b)]

$$\begin{aligned}S_1(t|x_0)e^{mt}=&(u_1+\sqrt{K_1}u_2)e^{K_1t}+u_2\left\{\frac{1}{\sqrt{\pi t}}-\sqrt{K_1}\Omega\left(\sqrt{K_1t}\right)\right\}\\&+\sum_{i=1}^{\infty}\frac{(2i-1)!!\varepsilon_{2i-1}}{(-2t)^i\sqrt{\pi t}},\end{aligned}\tag{27a}$$

$$\begin{aligned}S_2(t|x_0)e^{mt}=&(v_1+\sqrt{K_2}v_2)e^{K_2t}+v_2\left\{\frac{1}{\sqrt{\pi t}}-\sqrt{K_2}\Omega\left(\sqrt{K_2t}\right)\right\}\\&+\sum_{i=1}^{\infty}\frac{(2i-1)!!\phi_{2i-1}}{(-2t)^i\sqrt{\pi t}},\end{aligned}\tag{27b}$$

where $\Omega(y)=W(0,y)=\exp(y^2)\mathrm{erfc}(y)$ and $(2i-1)!!=(2i-1)(2i-3)\cdots 3\cdot 1$. Using the symmetric relation of the complementary error function,[17] one can easily obtain the long-time asymptotic form of $\Omega(y\sqrt{t})$ as [Eq. (28)]

$$\Omega(y\sqrt{t})\sim\begin{cases}\dfrac{1}{y\sqrt{\pi t}}-\dfrac{1}{2y^3t\sqrt{\pi t}}, & \text{when } |\arg\, y|<3\pi/4,\\ 2e^{y^2t}-\Omega(-y\sqrt{t}), & \text{when } |\arg\, y|>3\pi/4.\end{cases}\tag{28}$$

Substituting [Eq. (28)] into [Eq. (27a)] and [Eq. (27b)], the long-time asymptotic expressions of the survival probabilities can be obtained in the following forms [Eq. (29a)] and [Eq. (29b)]:

$$S_1(t|x_0)e^{mt} \sim A_1 e^{K_1 t} + B_1 t^{-3/2}, \tag{29a}$$

$$S_2(t|x_0)e^{mt} \sim A_2 e^{K_2 t} + B_2 t^{-3/2}, \tag{29b}$$

where A_i and B_i are the unknown coefficients to be determined. Note that one can find, from [Eq. (29a)] and [Eq. (29b)], that $S_i(t|x_0)\exp(mt)$ undergo a kinetic transition when the K_i values changes sign.

Determination of A_i Values

We now determine the unknown coefficients A_i and B_i by applying the method developed in the previous work.[8] First, we determine A_1 by taking the limit $s \to \min\{k_{u1}, k_{u2}+a_2^2 D_2\}$ as follows:

1) When $k_{u2}+a_2^2D_2 > k_{u1}$ (or $K_1>0$), by taking the limit $s_{u1}\to 0$, we get [Eq. (30a)]

$$\begin{aligned} A_1 &\equiv \lim_{s_{u1}\to 0} s_{u1}\hat{S}_1(s|x_0) = \lim_{t\to\infty} S_1(t|x_0)\exp(k_{u1}t) \\ &= 1 - \frac{[\alpha_1'(\alpha''_2+\sqrt{a_1^2D_1+K})-\alpha_1\alpha_2]\exp[2a_1H(-a_1)x_0]}{[\alpha_1'-2a_1\sqrt{D_1}H(-a_1)](\alpha''_2+\sqrt{a_1^2D_1+K})-\alpha_1\alpha_2}, \end{aligned} \tag{30a}$$

where $H(x)$ is the Heaviside step function [$H(x)=1$ when $x>0$ and $H(x)=0$ when $x<0$]. Note that $S_1(t|x_0)\exp(mt)$ undergoes a kinetic transition according to the sign of the applied field, a_1, because $A_1=0$ when $a_1>0$ and $A_1\neq 0$ when $a_1<0$.

2) When $k_{u2}+a_2^2D_2 < k_{u1}$ (or $K_1<0$), by taking the limit $s_2\to 0$, we get [Eq. (30b)]

$$\begin{aligned} &\lim_{s_2\to 0} s_2\hat{S}_1(s|x_0) = \lim_{t\to\infty} S_1(t|x_0)\exp[(k_{u2}+a_2^2D_2)t] \\ &\equiv \lim_{t\to\infty}\left[A_1\exp(K_1t)+B_1t^{-3/2}\right] = 0. \end{aligned} \tag{30b}$$

Because [Eq. (30b)] vanishes, it is safe to set $A_1=0$. Note that, in this case, $S_1(t|x_0)\exp(mt)$ follows a $t^{-3/2}$ power-law behavior.

Similarly, one can obtain A_2 by taking limit $s\to\min\{k_{u2}, k_{u1}+a_1^2D_1\}$ as follows:

1) When $k_{u1}+a_1^2D_1 > k_{u2}$ (or $K_2>0$), by taking limit $s_{u2}\to 0$, we get [Eq. (31a)]

$$\begin{aligned} A_2 &\equiv \lim_{s_{u2}\to 0} s_{u2}\hat{S}_2(s|x_0) = \lim_{t\to\infty} S_2(t|x_0)\exp(k_{u2}t) \\ &= -\frac{2\alpha_1a_2\sqrt{D_2}H(-a_2)\exp[(a_1\sqrt{D_1}-\sqrt{a_2^2D_2-K})x_0/\sqrt{D_1}]}{(\alpha''_1+\sqrt{a_2^2D_2-K})[\alpha''_2-2a_2\sqrt{D_2}H(-a_2)]-\alpha_1\alpha_2}. \end{aligned} \tag{31a}$$

Similarly to $S_1(t|x_0)\exp(mt)$ when $K_1>0$, $S_2(t|x_0)\exp(mt)$ undergoes a kinetic transition according to the sign of a_2 because $A_2=0$ when $a_2>0$ and $A_2\neq 0$ when $a_2<0$.

2) When $k_{u1}+a_1^2D_1 < k_{u2}$ (or $K_2<0$), by taking the limit $s_1\to 0$, we get [Eq. (31b)]

$$\begin{aligned} &\lim_{s_1\to 0} s_1\hat{S}_2(s|x_0) = \lim_{t\to\infty} S_2(t|x_0)\exp[(k_{u1}+a_1^2D_1)t] \\ &\equiv \lim_{t\to\infty}\left[A_2\exp(K_2t)+B_2t^{-3/2}\right] = 0. \end{aligned} \tag{31b}$$

Therefore, it is safe to set $A_2=0$. In this case, $S_2(t|x_0)\exp(mt)$ obeys a $t^{-3/2}$ power-law behavior.

In summary, we can determine A_i explicitly when $K_i>0$ while the A_i term is set to 0 when $K_i<0$.

Determination of B_i Values

Next, we need to evaluate the coefficients B_1 and B_2 for the asymptotic kinetics of the survival probabilities. From the asymptotic expansion of $\hat{S}_i(s|x_0)$ and the theory of the Laplace transform, we can obtain the coefficients of $t^{-3/2}$ (See Appendix B) as in previous work.[8]

From the series expansions of [Eq. (20a)] and [Eq. (20b)] in the region of $s=-m$, one obtains β_i, the coefficient of $\sqrt{s_m}$ [see Eq. (B2) in the Appendix]. We have two cases for β_i depending on the sign of K, $\beta_{i,j}$. The first subscript denotes the state of the geminate pair, $i=1$ or 2 for the A*B or C*D pair, respectively. The second subscript denotes the sign of K, $j=1$ or 2 for $K>0$ or $K<0$, respectively.

1) When $K>0$ [Eq. (32a)] and [Eq. (32b)],

$$\begin{aligned} \beta_{1,1} = &\frac{e^{a_1x_0}[\alpha_1'(\alpha''_2+\sqrt{K})-\alpha_1\alpha_2]}{\alpha_1'(\alpha''_2+\sqrt{K})-\alpha_1\alpha_2} \\ &\times\left[\frac{x_0}{\sqrt{D_1}}+\frac{\alpha''_2+\sqrt{K}}{\alpha''_1(\alpha''_2+\sqrt{K})-\alpha_1\alpha_2}\right], \end{aligned} \tag{32a}$$

$$\beta_{2,1} = \frac{e^{a_1x_0}\alpha_1(a_2\sqrt{D_2}-\sqrt{K})}{\alpha''_1(\alpha''_2+\sqrt{K})-\alpha_1\alpha_2}\left[\frac{x_0}{\sqrt{D_1}}+\frac{\alpha''_2+\sqrt{K}}{\alpha''_1(\alpha''_2+\sqrt{K})-\alpha_1\alpha_2}\right], \tag{32b}$$

2) When $K<0$ [Eq. (33a)] and [Eq. (33b)],

$$\beta_{1,2} = \frac{\alpha_1\alpha_2(a_1\sqrt{D_1}-\sqrt{|K|})}{[(\alpha''_1+\sqrt{|K|})\alpha''_2-\alpha_1\alpha_2]^2}\exp\left[\left(a_1-\sqrt{\frac{|K|}{D_1}}\right)x_0\right], \tag{33a}$$

$$\beta_{2,2} = \frac{\alpha_1[(\alpha''_1+\sqrt{|K|})\alpha''_2-\alpha_1\alpha_2]}{[(\alpha''_1+\sqrt{|K|})\alpha''_2-\alpha_1\alpha_2]^2}\exp\left[\left(a_1-\sqrt{\frac{|K|}{D_1}}\right)x_0\right]. \tag{33b}$$

By substituting [Eq. (32a)], [Eq. (32b)] and [Eq. (33a)], [Eq. (33b)] into [Eq. (B7) in the Appendix], one obtains the asymptotic behavior from [Eq. (B3)] as shown in [Eq. (34)]

$$S_i(t|x_0)\exp(mt) \sim A_i\exp(K_it) + \frac{\beta_{i,j}}{2K_i\sqrt{\pi}}t^{-3/2}. \tag{34}$$

Considering [Eq. (30a)], [Eq. (30b)], [Eq. (31a)], [Eq. (31b)], and [Eq. (34)], we find that the asymptotic behavior of the effective survival probability, $S_i(t|x_0)\exp(mt)$, shows rather complex kinetic transition behavior depending on the signs of a_i, K_i, and K. Moreover, in certain cases, the number of kinetic transitions reduces arising from the destructive interplay between the effects of the field and lifetimes. It should be noted that the above-mentioned complex kinetic transition behavior does not depend on the quenching rate coefficients which influence only the amplitudes of the long-time asymptotic behavior of the effective survival probabilities (A_i and $\beta_{i,j}$). The long-time asymptotic behavior of $S_i(t|x_0)\exp(mt)$ are summarized in Table 1 and Table 2.

In Figure 2, the time-dependence of the effective survival probability, $S_1(t|x_0)\exp(mt)$, and the magnitude of its deviation from $A_1\exp(K_1t)$, $|S_1(t|x_0)\exp(mt) - A_1\exp(K_1t)|$, are shown for the positive value of K. The kinetic transition is clearly shown depending on the sign of a_1 in Figure 2a) and the power-law component of the long-time behavior of $S_1(t|x_0)\exp(mt)$ is shown in Figure 2b).

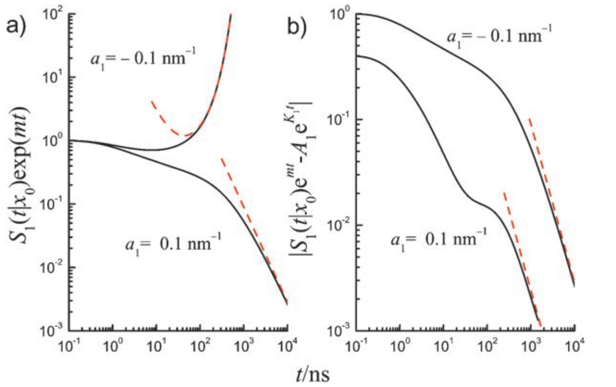

Figure 2. a) The time dependence of the effective survival probability, $S_1(t|x_0)e^{mt}$, and b) its magnitude of the deviation from $A_1e^{K_1t}$, $|S_1(t|x_0)e^{mt} - A_1e^{K_1t}|$, for positive values of K. The solid lines for the exact kinetics are taken from those in Figure 1a. The dashed lines are the long-time asymptotic behavior calculated from [Eq. (34)]. The values of the parameters are the same as those used in Figure 1a.

Destructive Interplay between the Effects of Field and Lifetimes

Recently, Kim and Shin investigated the geminate ES-ABC reaction with a constant external field in 1D.[7] They found that the number of kinetic transitions is found to be one or zero by varying the difference between the lifetimes. The latter case arises from the destructive interplay between the field intensity and lifetimes. By analogy, we also expect that the number of kinetic transitions in the present problem varies with changes in the applied field and lifetimes.

As was shown previously, the long-time asymptotic behavior of the effective survival probabilities, $S_i(t|x_0)\exp(mt)$, is given by [Eq. (34)]. For the state i, when $K_i < 0$, the first term on the right hand side of [Eq. (34)] decays exponentially. Thus, the kinetic transition depending on the sign of the applied field a_i disappears. Note that when two lifetimes are the same, there is no such destructive interplay.

The destructive interplay can be understood as follows. As the unimolecular decay rate (k_{ui}) for the given state i increases, the ES geminate pair in this state decays to the ground-state (GS) faster. Then, the lifetime effect on the state i overcomes those of the field and lifetime on the other state, j, when $K_i < 0$ (i.e., $k_{ui} > k_{uj} + a_j^2 D_j$ for $i,j = 1,2$ and $i \neq j$) and the first term $A_i\exp(K_it)$ of the effective survival probability in [Eq. (34)] vanishes regardless of the direction of the field.

Table 1. Long-time asymptotic behavior of $S_1(t|x_0)\exp(mt)$.

			$a_1 > 0$	$a_1 < 0$
$K > 0$	$K_1 > 0$	$S_1(t\mid x_0)e^{(k_{u1}+a_1^2D_1)t}$	$\frac{\beta_{1,1}t^{-3/2}}{2K_1\sqrt{\pi}}$	$A_1e^{a_1^2D_1t}+\frac{\beta_{1,1}t^{-3/2}}{2K_1\sqrt{\pi}}$
$K < 0$	$K_1 > 0$	$S_1(t\mid x_0)e^{(k_{u2}+a_2^2D_2)t}$	$\frac{\beta_{1,2}t^{-3/2}}{2K_1\sqrt{\pi}}$	$A_1e^{(a_1^2D_1+K)t}+\frac{\beta_{1,2}t^{-3/2}}{2K_1\sqrt{\pi}}$
	$K_1 < 0$		$\frac{\beta_{1,2}t^{-3/2}}{2K_1\sqrt{\pi}}$	

Table 2. Long-time asymptotic behavior of $S_2(t|x_0)\exp(mt)$.

			$a_2 > 0$	$a_2 < 0$
$K > 0$	$K_2 > 0$	$S_2(t\mid x_0)e^{(k_{u1}+a_1^2D_1)t}$	$\frac{\beta_{2,1}t^{-3/2}}{2K_2\sqrt{\pi}}$	
	$K_2 > 0$		$\frac{\beta_{2,1}t^{-3/2}}{2K_2\sqrt{\pi}}$	$A_2e^{(a_2^2D_2-K)t}+\frac{\beta_{2,1}t^{-3/2}}{2K_2\sqrt{\pi}}$
$K < 0$	$K_2 < 0$	$S_2(t\mid x_0)e^{(k_{u2}+a_2^2D_2)t}$	$\frac{\beta_{2,2}t^{-3/2}}{2K_2\sqrt{\pi}}$	$A_2e^{a_2^2D_2t}+\frac{\beta_{2,2}t^{-3/2}}{2K_2\sqrt{\pi}}$

In Figure 3, the time-dependence of the effective survival probability $S_1(t|x_0)\exp(mt)$ is shown for a negative value of K_1. In comparison to Figure 2a, the destructive interplay between the applied field and lifetimes is clearly shown in this figure.

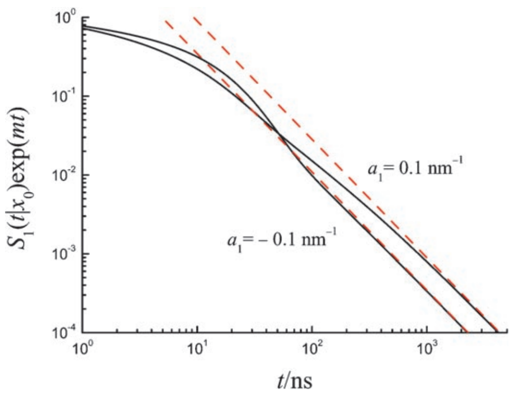

Figure 3. The time dependence of the effective survival probability, $S_1(t|x_0)e^{mt}$, for negative value of K_1. The dashed lines are the long-time asymptotic behavior calculated from [Eq. (34)]. The values of the parameters are the same as those used in Figure 1 except $k_{u1}=0.2\ \mathrm{ns}^{-1}$ and $a_2=0.1\ \mathrm{nm}^{-1}$.

Asymptotic Behavior when $a_i=0$

For the geminate GS-ABCD reaction under a constant external field,[8] we found that the long-time asymptotic behaviors of the survival probabilities become simpler when one of the a_i's vanishes, that is, simple $t^{-1/2}$ power-law behaviors appear. Now we investigate the long-time asymptotic behaviors of the effective survival probabilities in this case for the present problem.

Case 1. $a_1=0$.

In this case, $K=\Delta k_u + a_2^2 D_2$ ($\Delta k_u \equiv k_{u2}-k_{u1}$) and A_1 vanishes. Then, the long-time asymptotic behavior of $S_1(t|x_0)$ is changed as follows. When $K>0$ ($m=k_{u1}$ or $K_1=0$), [Eq. (B2) of the Appendix] can be rewritten as [Eq. (35a)]

$$s_{u1}\hat{S}_1(s|x_0) \sim \beta_{1,1}\sqrt{s_{u1}}, \tag{35a}$$

that is, $S_1(t|x_0)\exp(k_{u1}t)$ behaves asymptotically as [Eq. (35b)]

$$S_1(t|x_0)\exp(k_{u1}t) \sim \beta_{1,1}/\sqrt{\pi t}. \tag{35b}$$

However, when $K<0$ ($K_1<0$), the asymptotic kinetics follows [Eq. (34)] with a vanishing A_1 value(see [Eq. (30b)]) and $S_1(t|x_0)\exp(mt)$ shows a $t^{-3/2}$ power-law asymptotic behavior. Therefore, $S_1(t|x_0)\exp(mt)$ undergoes a kinetic transition behavior from $t^{-3/2}$ to $t^{-1/2}$ power-law as K changes from a negative to a positive value.

On the other hand, the asymptotic kinetics of $S_2(t|x_0)\exp(mt)$ can be obtained from [Eq. (34)] for both cases of $K>0$ and $K<0$. Note that the destructive interplay occurs for $S_2(t|x_0)\exp(mt)$ when $\Delta k_u>0$ ($K_2<0$), which shows a $t^{-3/2}$ power-law behavior for both negative and positive values of a_2.

Case 2. $a_2=0$.

In this case $K=\Delta k_u - a_1^2 D_1$ and A_2 vanishes. Analogously to case 1, when $K<0$, [Eq. (B2) of the Appendix] can be rewritten as [Eq. (36a)]

$$s_{u2}\hat{S}_2(s|x_0) \sim \beta_{2,2}\sqrt{s_{u2}}, \tag{36a}$$

that is, $S_2(t|x_0)\exp(k_{u2}t)$ behaves asymptotically as [Eq. (36b)]

$$S_2(t|x_0)\exp(k_{u2}t) \sim \beta_{2,2}/\sqrt{\pi t}. \tag{36b}$$

When $K>0$ ($K_2<0$), the asymptotic kinetics follows [Eq. (34)] with a vanishing A_2 value (see [Eq. (31b)]) and the kinetics of $S_2(t|x_0)\exp(mt)$ shows a $t^{-3/2}$ power-law asymptotic behavior. Therefore, $S_2(t|x_0)\exp(mt)$ obeys $t^{-1/2}$ and $t^{-3/2}$ power-law behavior when $K<0$ and $K>0$, respectively. On the other hand, $S_1(t|x_0)\exp(mt)$ follows [Eq. (34)] and shows the destructive interplay when $\Delta k_u<0$ ($K_1<0$), following $t^{-3/2}$ power-law behaviour for both negative and positive values of a_1.

When both $a_1=0$ and $a_2=0$, the kinetics reduces to that of the geminate ES-ABCD reaction without a field, that is, when $k_{u1}<k_{u2}$, $S_1(t|x_0)\exp(k_{u1}t)$ obeys $t^{-1/2}$ power-law asymptotic behavior, whereas $S_1(t|x_0)\exp(k_{u2}t)$ follows a $t^{-3/2}$ power-law when $k_{u1}>k_{u2}$.[12]

In. Figure 4, the time-dependence of the effective survival probability $S_1(t|x_0)\exp(mt)$ is plotted when $a_1=0$. The kinetic transition from $t^{-3/2}$ to $t^{-1/2}$ power-law behavior is clearly seen as K changes its sign.

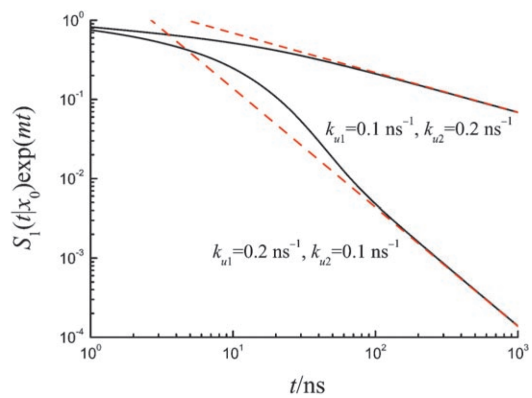

Figure 4. The time dependence of the effective survival probability $S_1(t|x_0)e^{mt}$ for vanishing a_1 depending on the sign of K: $K>0$ ($k_{u1}=0.1\ \mathrm{ns}^{-1}$ and $k_{u2}=0.2\ \mathrm{ns}^{-1}$) and $K<0$ ($k_{u1}=0.2\ \mathrm{ns}^{-1}$ and $k_{u2}=0.1\ \mathrm{ns}^{-1}$). The dotted lines are the long-time asymptotic behavior calculated from [Eq. (34)] and [Eq. (35b)]. The values of the other parameters are the same as those used in Figure 1 except $D_2=1.0\ \mathrm{nm}^2/\mathrm{ns}$.

Conclusions

We obtained the exact Green functions for the geminate ES-ABCD reaction in the presence of quenching processes under a constant external field in 1D in the Laplace domain. With these exact Green functions, we also obtained the survival probabilities for the reactant and product states. The analytic expressions in the time domain could only be obtained for the case when $K=0$. However, we could obtain analytic short-time approximations which are valid for $t<|K|^{-1}$ and the long-time asymptotic expressions, which allowed us to analytically investigate the effect of the field and lifetimes on these survival probabilities.

By analyzing the long-time asymptotic behavior, we find that the effective survival probability, $S_i(t|x_0)\exp(mt)$, shows a rather complex kinetic transition behavior depending on the sign of the intensity of the external field a_i. The destructive interplay between the lifetimes and field occurs when the lifetime effect on one state exceeds the field and lifetime effects on the other state ($K_i<0$). In this case, the kinetic transition, which depends on the sign of a_i, disappears. When one of the field effect vanishes, for example, $a_1=0$, the effective survival probability, $S_1(t|x_0)\exp(mt)$, obeys a $t^{-1/2}$ asymptotic power-law behavior when $K>0$, whereas it follows a $t^{-3/2}$ power-law when $K<0$.

The above-mentioned complex kinetic transition behavior does not depend on the quenching rate coefficients which only influence the amplitudes of the long-time asymptotic behaviors of the effective survival probabilities.

Because the Green functions for a geminate problem can be utilized in the simulations[14] and the theory of the corresponding many-body problem,[15] our Green functions may have applicability to more general cases. Also, the field and lifetime effects investigated in this work may help us to understand the rich kinetics of ABCD reaction, which may be found in relevant experiments.

Appendix A.

Exact Green Function when K = 0

Let us define the transformation[18] [Eq. (A1)]

$$q_i(x_i,t|x_0)=\exp(a_ix_i-a_1x_0+a_i^2D_it+k_{ui}t)p_i(x_i,t|x_0) \tag{A1}$$

and $\xi\equiv s_1=s_2$. Then, the GFs from [Eq. (18a)] and [Eq. (18b)] can be rewritten as [Eq. (A2a)] and [Eq. (A2b)]

$$\hat{q}_1(x_1,\xi|x_0)=\hat{F}_1(x_1,\xi|x_0)-\frac{[\alpha_1'(\sqrt{\xi}+\alpha_2'')-\alpha_1\alpha_2]\exp[-\sqrt{\xi/D_1}(x_1+x_0)]}{\sqrt{D_1}(\sqrt{\xi}-a_1\sqrt{D_1})(\sqrt{\xi}+\sigma_1)(\sqrt{\xi}+\sigma_2)}, \tag{A2a}$$

$$\hat{q}_2(x_2,\xi|x_0)=\frac{\alpha_1\exp[-\sqrt{\xi/D_2}x_2-\sqrt{\xi/D_1}x_0]}{\sqrt{D_2}(\sqrt{\xi}+\sigma_1)(\sqrt{\xi}+\sigma_2)}, \tag{A2b}$$

where the σ_i terms are defined in [Eq. (23)].

[Eq (A2a)] and [Eq. (A2b)] can now be analytically inverted into the time domain to give [Eq. (A3a)] and [Eq. (A3b)]

$$\begin{aligned}q_1(x_1,t|x_0)=&F_1(x_1,t|x_0)\\&+\frac{1}{\sqrt{D_1}}\left\{\frac{\sigma_2[\alpha_1'(\alpha_2''-\sigma_2)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_2+a_1\sqrt{D_1})}W(\chi_1+\chi_0,\sigma_2\sqrt{t})\right.\\&\left.-\frac{\sigma_1[\alpha_1'(\alpha_2''-\sigma_1)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_1+a_1\sqrt{D_1})}W(\chi_1+\chi_0,\sigma_1\sqrt{t})\right\}\\&-a_1W\left(\chi_1+\chi_0,-a_1\sqrt{D_1t}\right),\end{aligned} \tag{A3a}$$

$$q_2(x_2,t|x_0)=-\frac{\sigma_1}{\sigma_2-\sigma_1}W(\chi_2+\chi_0,\sigma_1\sqrt{t})\Big], \tag{A3b}$$

where $\chi_0=x_0/\sqrt{4D_1t}$, $\chi_i=x_i/\sqrt{4D_it}$ $(i=1,2)$, and [Eq. (A3c)]

$$\begin{aligned}F_1(x_1,t|x_0)=&\frac{1}{2\sqrt{\pi D_1t}}[e^{-(\chi_1-\chi_0)^2}+e^{-(\chi_1+\chi_0)^2}]\\&+a_1W\left(\chi_1+\chi_0,-a_1\sqrt{D_1t}\right).\end{aligned} \tag{A3c}$$

Let us define the effect survival probabilities, $S_i'(t|x_0)$, as [Eq. (A4)]

$$S_i'(t|x_0)=S_i(t|x_0)\exp(mt). \tag{A4}$$

Then, these effective survival probabilities in the Laplace domain can be written as [Eq. (A5a)] and [Eq. (A5b)]

$$1-(\xi-a_1^2D_1)\hat{S}_1'(\xi|x_0)=\frac{\alpha_1'(\sqrt{\xi}+\alpha_2'')-\alpha_1\alpha_2}{(\sqrt{\xi}+\sigma_1)(\sqrt{\xi}+\sigma_2)}\exp\left[\left(a_1-\sqrt{\frac{\xi}{D_1}}\right)x_0\right], \tag{A5a}$$

$$(\xi-a_2^2D_2)\hat{S}_2'(\xi|x_0)=\frac{\alpha_1(\sqrt{\xi}-a_2\sqrt{D_2})}{(\sqrt{\xi}+\sigma_1)(\sqrt{\xi}+\sigma_2)}\exp\left[\left(a_1-\sqrt{\frac{\xi}{D_1}}\right)x_0\right]. \tag{A5b}$$

In the time domain, $S_i'(t|x_0)$ are obtained by the direct integration of [Eq. (A3a)] and [Eq. (A3b)] or inversion of [Eq. (A5a)] and [Eq. (A5b)] as [Eq. (A6a)] and [Eq. (A6b)]

$$\begin{aligned}\frac{S_1'(t|x_0)-e^{a_1^2D_1t}}{e^{a_1x_0}}=&\frac{\sigma_1[\alpha_1'(\alpha_2''-\sigma_1)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_1^2-a_1^2D_1)}W(\chi_0,\sigma_1\sqrt{t})\\&-\frac{\sigma_2[\alpha_1'(\alpha_2''-\sigma_2)-\alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_2^2-a_1^2D_1)}W(\chi_0,\sigma_2\sqrt{t})\\&-\frac{\alpha_1'(\alpha_2''-a_1\sqrt{D_1})-\alpha_1\alpha_2}{2(\sigma_1-a_1\sqrt{D_1})(\sigma_2-a_1\sqrt{D_1})}W\left(\chi_0,a_1\sqrt{D_1t}\right)\\&-\frac{1}{2}W\left(\chi_0,-a_1\sqrt{D_1t}\right),\end{aligned} \tag{A6a}$$

$$\frac{S_2'(t|x_0)}{\alpha_1 e^{a_1 x_0}} = \frac{\sigma_1 W(\chi_0, \sigma_1\sqrt{t})}{(\sigma_2-\sigma_1)(\sigma_1 - a_2\sqrt{D_2})} - \frac{\sigma_2 W(\chi_0, \sigma_2\sqrt{t})}{(\sigma_2-\sigma_1)(\sigma_2 - a_2\sqrt{D_2})} - \frac{a_2\sqrt{D_2}W(\chi_0, a_2\sqrt{D_2 t})}{(\sigma_1 - a_2\sqrt{D_2})(\sigma_2 - a_2\sqrt{D_2})}. \tag{A6b}$$

Using the symmetric relation of the complementary error function,[17] we find that the long-time asymptotic behaviors are obtained as follows [Eq. (A7a)] and [Eq. (A7b)]:

$$\begin{aligned}\frac{S_1'(t|x_0) - e^{a_1^2 D_1 t}}{e^{a_1 x_0}} \sim & \frac{2\sigma_1[\alpha_1'(\alpha''_2-\sigma_1) - \alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_1^2 - a_1^2 D_1)} e^{\sigma_1^2 t + \sigma_1 x_0/\sqrt{D_1}} H(-\sigma_1) \\ & - \frac{2\sigma_2[\alpha_1'(\alpha''_2-\sigma_2) - \alpha_1\alpha_2]}{(\sigma_2-\sigma_1)(\sigma_2^2 - a_1^2 D_1)} e^{\sigma_2^2 t + \sigma_2 x_0/\sqrt{D_1}} H(-\sigma_2) \\ & - \frac{\alpha_1'(\alpha''_2 - a_1\sqrt{D_1}) - \alpha_1\alpha_2}{(\sigma_1 - a_1\sqrt{D_1})(\sigma_2 - a_1\sqrt{D_1})} e^{a_1^2 D_1 t + a_1 x_0} H(-a_1) \\ & - e^{a_1^2 D t - a_1 x_0} H(a_1) \\ & + \left(\frac{x_0}{\sqrt{D_1}} + \frac{\sigma_1+\sigma_2}{\sigma_1\sigma_2} - \frac{\alpha_1'}{\alpha_1'\alpha''_2 - \alpha_1\alpha_2}\right) \frac{\alpha_1'\alpha''_2 - \alpha_1\alpha_2}{2\sigma_1\sigma_2 a_1^2 D_1 t\sqrt{\pi t}},\end{aligned} \tag{A7a}$$

$$\begin{aligned}\frac{S_2'(t|x_0)}{\alpha_1 e^{a_1 x_0}} \sim & \frac{2\sigma_1 e^{\sigma_1^2 t + \sigma_1 x_0/\sqrt{D_1}} H(-\sigma_1)}{(\sigma_2-\sigma_1)(\sigma_1 - a_2\sqrt{D_2})} - \frac{2\sigma_2 e^{\sigma_2^2 t + \sigma_2 x_0/\sqrt{D_1}} H(-\sigma_2)}{(\sigma_2-\sigma_1)(\sigma_2 - a_2\sqrt{D_2})} \\ & - \frac{2a_2\sqrt{D_2} e^{a_2^2 D_2 t + a_2 x_0\sqrt{D_2/D_1}} H(-a_2)}{(\sigma_1 - a_2\sqrt{D_2})(\sigma_2 - a_2\sqrt{D_2})} \\ & + \left(\frac{x_0}{\sqrt{D_1}} + \frac{\sigma_1+\sigma_2}{\sigma_1\sigma_2} + \frac{1}{a_2\sqrt{D_2}}\right)\frac{1}{2\sigma_1\sigma_2 a_2 t\sqrt{\pi D_2 t}}.\end{aligned} \tag{A7b}$$

Appendix B

Determination of the Coefficient of the $t^{-3/2}$-Term Long-Time Asymptotic Expansion of $S_i(t|x_0)\exp(mt)$ when $K \neq 0$

From the theory of Laplace transform,[17] we can write $s_{ui}\hat{S}_i(s|x_0) - S_i(0|x_0)$ as [Eq. (B1)]

$$(s_m - K_i)\hat{S}_i(s_m - m|x_0) - S_i(0|x_0) = \int_0^\infty dt\, e^{-(s_m-K_i)t} \frac{d}{dt}\left[S_i(t|x_0)e^{k_{ui}t}\right]. \tag{B1}$$

By taking the limit $s_m \to 0$ and expanding the right side of [Eq. (20a)] and [Eq. (20b)], one finds that the asymptotic form of the left side of [Eq. (B1)] is given by the functional form as [Eq. (B2)]

$$(s_m - K_i)\hat{S}_i(s_m - m|x_0) - S_i(0|x_0) \sim \beta_i\sqrt{s_m}, \tag{B2}$$

where β_i is a field dependent coefficient.

On the other hand, one can rewrite [Eq. (27a)] and [Eq. (27b)] as [Eq. (B3)]

$$S_i(t|x_0)\exp(mt) = A_i\exp(K_i t) + \sum_{j=1}^{\infty}\gamma_{i,j}t^{-(j+1/2)}, \tag{B3}$$

where $\gamma_{i,j}$ terms are field dependent coefficients to be determined. [Eq. (B3)] can be rewritten as [Eq. (B4)]

$$S_i(t|x_0)\exp(k_{ui}t) = A_i + \sum_{j=1}^{\infty}\gamma_{i,j}t^{-(j+1/2)}\exp(-K_i t). \tag{B4}$$

By differentiating [Eq. (B4)] and using the fact that A_i is independent of t, one obtains [Eq. (B5)]

$$\frac{d}{dt}[S_i(t|x_0)\exp(k_{ui}t)] = -\sum_{j=1}^{\infty}\gamma_{i,j}\left[K_i + (j+1/2)t^{-1}\right]t^{-(j+1/2)}\exp(-K_i t), \tag{B5}$$

which can be asymptotically written as [Eq. (B6)]

$$\frac{d}{dt}[S_i(t|x_0)\exp(k_{ui}t)] \sim -\gamma_{i,1}K_i t^{-3/2}\exp(-K_i t). \tag{B6}$$

By substituting [Eq. (B2)] and [Eq. (B6)] into [Eq. (B1)], we obtain the desired relation [Eq. (B7)]

$$\gamma_{i,1} = \frac{\beta_i}{2K_i\sqrt{\pi}}. \tag{B7}$$

Because we already know the expressions of A_i given in [Eq. (30a)], [Eq. (30b)] and [Eq. (31a)], [Eq. (31b)], we can determine the asymptotic behavior without explicitly determining the unknown coefficients in [Eq. (27a)] and [Eq. (27b)]. The coefficients for higher order terms in t can be determined by keeping more terms in [Eq (B2)] and [Eq. (B3)].

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