

## Direct Calculation Method for Excited-state Diffusion-influenced Reversible Reactions with an External Field<sup>†</sup>

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The direct calculation method is generalized to the excited-state diffusion-influenced reversible reaction of a neutral and a charged particle under an external field with two different lifetimes and quenching in three dimensions. The present method provides an alternative way to calculate the binding probability density functions and the survival probabilities from the corresponding irreversible results. The solutions are obtained as the series solutions by the diagonal approximation due to the anisotropy of the unidirectional external field. The numerical results are found to be in good agreement with those of the previous study [S. Y. Reigh *et al.* J. Chem. Phys. **132**, 164112 (2010)] within a weak field limit. The solutions of two approaches show qualitatively the same overall behavior including the power laws at long times.

**Key Words** : Reversible reaction, External field, Reaction-diffusion systems, Excited state reaction, Anisotropy

### Introduction

The diffusion-influenced reaction plays a significant role in a broad range of research fields.<sup>1</sup> The enzyme-substrate reaction is one of biologically interesting subjects. The time dependent kinetics on Michaelis-Menten mechanism<sup>2-4</sup> and the ligand binding to the receptors are often controlled by the diffusion.<sup>5,6</sup> The electron or energy transfer reaction in solutions is important in electrochemistry<sup>7-9</sup> and the proton transfer reaction is ubiquitous in the field of organic chemistry.<sup>10-12</sup> Numerous dynamical properties of soft matter systems such as the interactions of colloid particles or the reaction of polymers in solution depend on the diffusion-influenced reaction.<sup>13-15</sup> The migration of charged particle in a semiconductor is under control by the diffusion process.<sup>16</sup> It has been known that the diffusion-influenced reaction is frequently affected by the external field.<sup>16-28</sup> The gravitation is inevitable in the sedimentation of colloid particles<sup>21,22</sup> and the magnetic field can be applied to the migration of charged particles in a semiconductor.<sup>16</sup>

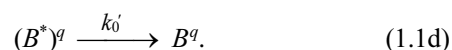
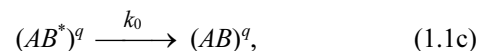
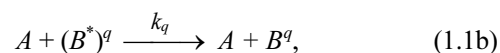
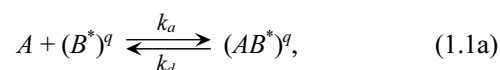
Recently, the external field effects on diffusion-influenced reversible reactions have been theoretically investigated in three dimensions.<sup>27,28</sup> These approaches were based on the Smoluchowski type equations of the probability density functions. Interestingly, it had been shown that the probability density functions or the survival probabilities can be directly calculated by setting up the kinetic equations for the relations between irreversible and reversible reactions.<sup>29-31</sup> However, this method is limited to the ground-state reversible reaction.<sup>29</sup> Hence, it is the intriguing problem to extend this direct calculation method to the excited-state reversible

reaction with two different unimolecular decay rates and quenching.

The paper is organized as follows: In Section II, the detailed procedure for deriving the solutions for an initially bound and a separated pair will be revealed. The solutions of the direct method and the previous study are compared and it will be shown that two solutions are converged to the same within a certain limit. The numerical result is shown in Section III and the conclusions are followed in Section IV.

### Theory and Solution

We consider two Brownian particles under a constant external field in three dimensions. One is a neutral particle  $A$  and the other is an excited charged particle  $(B^*)^q$  with a charge  $q$ . When two particles collide, they become the excited-state bound pair  $(AB^*)^q$  with the intrinsic rate constant  $k_a$ . The bound pair can dissociate reversibly into the original unbound pair of  $A$  and  $(B^*)^q$  with the rate constant  $k_d$ . The excited bound and unbound particles,  $(AB^*)^q$  and  $(B^*)^q$ , can decay to their ground-states with the unimolecular rate constants,  $k_0$  and  $k_0'$ , respectively. In addition,  $(B^*)^q$  can be quenched to  $B^q$  by  $A$  with the rate constant  $k_q$ . The reaction mechanism can be schematically written as



The particle  $A$  can be considered to be fixed at the origin

<sup>†</sup>This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

without loss of generality. We take the  $z$  axis along the same direction of the electric field  $\mathbf{E}$  if  $q$  is positive and along the reverse direction if  $q$  is negative. The system is symmetric about the azimuthal angle in the spherical polar coordinate.

**An Initially Bound Pair.** The global binding probability density function  $p(*, \tau|*)$  is obtained from the local binding probability density  $\rho(*, \mu, \tau|*, \mu_0)$  by averaging over the initial angle and taking the surface integral over the reaction surface.  $\rho(r, \mu, \tau|*, \mu_0)$  is the probability density function to observe the particle ( $B^*$ )<sup>q</sup> at a distance  $r$  and an angle  $\mu$  at time  $\tau = Dt$  for an initially bound particle ( $AB^*$ )<sup>q</sup> with an angle  $\mu_0$ . Here,  $*$  denotes the bound state. The probability density function  $p(*, \tau|*)$  and the survival probability  $S_{rev}(\tau|*)$  for the reversible reaction satisfy the following equations:

$$\frac{dp(*, \tau|*)}{d\tau} = k_a p(a, \tau|*) - (k_d + k_0) p(*, \tau|*), \quad (1.2)$$

$$\int_0^\tau k_d p(*, \tau'|*) K_{irr}(\tau - \tau'|a) d\tau' = (k_a + k_q) p(a, \tau|*), \quad (1.3)$$

$$\int_0^\tau k_d p(*, \tau'|*) S_{irr}(\tau - \tau'|a) d\tau' = S_{rev}(\tau|*), \quad (1.4)$$

$$p(*, \tau=0|*) = 1, \quad (1.5)$$

where  $p(*, \tau|*) = 1 - S_{rev}(\tau|*)$  and  $K_{irr}(\tau|a) = -\partial S_{irr}(\tau|a) / \partial \tau - k_0' S_{irr}(\tau|a)$  with the reaction distance  $a$ .  $K_{irr}$  and  $S_{irr}$  are the rate of reaction and the survival probability, respectively, for the irreversible reaction ( $k_d = 0$ ). By taking the Laplace transform [ $\tilde{f}(s) = \int_0^\infty f(\tau) e^{-s\tau} d\tau$ ], we obtain the following expressions:

$$\tilde{p}(*, s|*) = \frac{k_a + k_q}{(k_a + k_q)(s + k_d + k_0) - k_d k_d + k_a k_d (s + k_0')} \tilde{S}_{irr}(s|a), \quad (1.6)$$

$$\tilde{S}_{rev}(s|*) = \frac{k_d (k_a + k_q) \tilde{S}_{irr}(s|a)}{(k_a + k_q)(s + k_d + k_0) - k_d k_d + k_a k_d (s + k_0')} \quad (1.7)$$

We can easily confirm that two equations satisfy the normalization condition,

$$(s + k_0) \tilde{p}(*, s) + (s + k_0') \tilde{S}_{rev}(s) + k_q \tilde{p}(a, s) = 1. \quad (1.8)$$

The survival probability of the separated pair at time  $\tau$  with the initial separation  $\mathbf{r}_0$  for the irreversible reaction is calculated by the following Smoluchowski type equations:<sup>30,32</sup>

$$\frac{\partial S_{irr}(\tau|r_0, \mu_0)}{\partial \tau} = \nabla_{\mathbf{r}_0}^2 S_{irr} - \nabla_{\mathbf{r}_0} W_0 \cdot \nabla_{\mathbf{r}_0} S_{irr} - k_0' S_{irr}(\tau|r_0, \mu_0), \quad (1.9)$$

$$S_{irr}(\tau=0|r_0, \mu_0) = 1, \quad (1.10)$$

$$\left. \frac{\partial S_{irr}(\tau|r_0, \mu_0)}{\partial r_0} \right|_{r_0=a} = (k_a + k_q) S_{irr}(\tau|a, \mu_0), \quad (1.11)$$

$$\lim_{r_0 \rightarrow \infty} S_{irr}(\tau|r_0, \mu_0) = e^{-k_0' \tau}, \quad (1.12)$$

where  $W_0 = -2Fr_0\mu_0$  with the field constant  $F$ .<sup>27,28</sup> If we take the transformation as

$$S_{irr}(\tau|r_0, \mu_0) = e^{W_0/2} h(\tau|r_0, \mu_0), \quad (1.13)$$

we obtain the following equations:

$$\frac{\partial h}{\partial \tau} = \nabla_{\mathbf{r}_0}^2 h - (F^2 + k_0') h(\tau|r_0, \mu_0), \quad (1.14)$$

$$\left. \frac{\partial h}{\partial r_0} \right|_{r_0=a} = (k_a + k_q + F\mu_0) h(\tau|a, \mu_0), \quad (1.15)$$

$$h(\tau=0|r_0, \mu_0) = e^{Fr_0\mu_0}, \quad (1.16)$$

$$\lim_{r_0 \rightarrow \infty} e^{-Fr_0\mu_0} h(\tau|r_0, \mu_0) = e^{-k_0' \tau}. \quad (1.17)$$

We can separate the angular and the radial part of  $h(\tau|r_0, \mu_0)$  in Eq. (1.14) as

$$h(\tau|r_0, \mu_0) = \sum_{l=0}^{\infty} A_l P_l(\mu_0) R_l(\tau|r_0), \quad (1.18)$$

where  $P_l(\mu_0)$  is the Legendre function and  $R_l(\tau|r_0)$  satisfies

$$\frac{\partial R_l(\tau|r_0)}{\partial \tau} = \frac{\partial^2 R_l}{\partial r^2} + \frac{2}{r} \frac{\partial R_l}{\partial r} - \left[ F^2 + k_0' + \frac{\lambda_l}{r^2} \right] R_l(\tau|r_0). \quad (1.19)$$

From the initial condition of Eq. (1.16) and the relation

$$e^{Fr_0\mu_0} = \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) \sqrt{\frac{\pi}{2Fr_0}} I_{l+1/2}(Fr_0), \quad (1.20)$$

the normalization constant  $A_l$  and the initial condition for  $R_l$  are given by  $A_l = (2l+1)$  and  $R_l(\tau=0|r_0) = \sqrt{\pi/(2Fr_0)} I_{l+1/2}(Fr_0)$ , respectively. The Laplace transform of Eq. (1.19) gives two linearly independent homogenous solutions of the modified spherical Bessel functions as  $y_{1l}$  and  $y_{2l}$ ,

$$y_{1l}(r, s) = \sqrt{\frac{\pi}{2\sigma r}} I_{l+1/2}(\sigma r), \quad (1.21)$$

$$y_{2l}(r, s) = \sqrt{\frac{\pi}{2\sigma r}} K_{l+1/2}(\sigma r), \quad (1.22)$$

where  $\sigma = \sqrt{s + F^2 + k_0'}$ .<sup>33</sup> Using the outer boundary condition Eq. (1.17), the general solution of the nonhomogeneous equation with the particular solution,  $y_{1l}(r_0, s = -k_0')/(s + k_0')$ , is obtained by

$$\tilde{R}_l(s|r_0) = \frac{1}{s + k_0'} [y_{1l}(r_0, s = -k_0') - \alpha_l y_{2l}(r_0, s)]. \quad (1.23)$$

The use of the angle-dependent inner boundary condition, Eq. (1.15) allows us to determine the coefficient  $\alpha_l$  as the infinite tridiagonal matrix equation,

$$\begin{pmatrix} D_0 & E_{20} & & & \\ E_{11} & D_1 & E_{21} & & \\ & E_{12} & D_2 & E_{22} & \\ & & & \ddots & \\ & & & E_{1l} & D_l & E_{2l} \\ & & & & & \ddots \end{pmatrix} \begin{pmatrix} \alpha_0 \\ \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_l \\ \vdots \end{pmatrix} = \begin{pmatrix} L_0 + E_{40} \\ E_{31} + L_1 + E_{41} \\ E_{32} + L_2 + E_{42} \\ \vdots \\ E_{3l} + L_l + E_{4l} \\ \vdots \end{pmatrix}, \quad (1.24)$$

where  $D_l = (k_a + k_q) y_{2l}(a, s) - y_{2l}'(a, s)$ ,

$L_l = (k_a + k_q) y_{1l}(a, s = -k_0') - y_{1l}'(a, s = -k_0')$ ,

$$E_{1l} = F \frac{l}{2l+1} y_{2,l-1}(a,s), \quad E_{2l} = F \frac{l+1}{2l+1} y_{2,l+1}(a,s),$$

$$E_{3l} = F \frac{l}{2l+1} y_{1,l-1}(a,s = -k'_0), \quad \text{and} \quad E_{4l} = F \frac{l+1}{2l+1} y_{1,l+1}(a,s = -k'_0).$$

If we assume that  $\frac{E_{il}}{D_l}$  ( $i = 1, \dots, 4$ ) is small enough, we obtain  $\alpha_l$  as

$$\alpha_l \cong \frac{(k_a + k_q)y_{1l}(a,s = -k'_0) - y'_{1l}(a,s = -k'_0)}{(k_a + k_q)y_{2l}(a,s) - y'_{2l}(a,s)} + \mathcal{O}\left(\frac{E_{il}}{D_l}\right). \quad (1.25)$$

Therefore, we get the analytic solution of the survival probability for the irreversible reaction in the Laplace domain as

$$\tilde{S}_{irr}(s|r_0, \mu_0) = e^{-Fr_0\mu_0} \frac{1}{s+k'_0} \sum_{l=0}^{\infty} (2l+1) [y_{1l}(r_0, s = -k'_0) - \alpha_l y_{2l}(r_0, s)] P_l(\mu_0). \quad (1.26)$$

Averaging  $\tilde{S}_{irr}(s|r_0, \mu_0)$  over the initial angle  $\mu_0$  [ $\tilde{S}_{irr}(s|r_0) = \int_{-1}^1 d\mu_0 \tilde{S}_{irr}(s|r_0, \mu_0) / 2$ ], we obtain

$$\tilde{S}_{irr}(s|r_0) = \frac{1}{s+k'_0} \sum_{l=0}^{\infty} (-1)^l (2l+1) [y_{1l}(r_0, s = -k'_0) - \alpha_l y_{2l}(r_0, s)] \times y_{1l}(a, s = -k'_0). \quad (1.27)$$

The  $l = 0$  term of Eq. (1.27) is given by

$$\tilde{S}_{irr,l=0}(s|r_0) = \frac{1}{s+k'_0} \left[ \Xi + \Psi \frac{\sigma_1 + F\gamma a}{\sigma - \sigma_1 r_0} e^{-\sigma(r_0 - a)} \right], \quad (1.28)$$

where  $\Xi = y_{10}(a, s = -k'_0) y_{10}(r_0, s = -k'_0)$ ,  $\Psi = y_{10}^2(a, s = -k'_0)$ , and  $\gamma = \coth(Fa)$ . Thus, the expression  $\tilde{S}_{irr}(s|a)$  in Eq. (1.6) can be obtained from Eq. (1.28) to give

$$\tilde{S}_{irr,l=0}(s|a) = \frac{\Psi(\sigma + F\gamma)}{(s+k'_0)(\sigma - \sigma_1)}, \quad (1.29)$$

where  $\sigma_1 = -(k_a + k_q + 1/a)$ . Therefore, we obtain  $\tilde{p}_{l=0}(*, s|*)$  and  $\tilde{S}_{rev,l=0}(s|*)$  from Eqs. (1.6) and (1.7) as follows:

$$\tilde{p}_{l=0}(*, s|*) = \frac{\sigma - \sigma_1}{\Delta_0'(\sigma)}, \quad (1.30)$$

$$\tilde{S}_{rev,l=0}(s|*) = \frac{\Psi k_a (\sigma + F\gamma)}{(\sigma^2 - F^2) \Delta_0'(\sigma)}, \quad (1.31)$$

where  $\Delta_0'(\sigma) = \Delta_0(\sigma) + \{(\Psi - 1)\sigma + (\Psi F\gamma - 1/a)\} k_a k_d / (k_a + k_q)$ ,  $\Delta_0(\sigma) = (\sigma - \sigma_1)(\sigma^2 - \sigma_2) - k_a k_d$ , and  $\sigma_2 = F^2 - k_d + k'_0 - k_0$ .

Now, we can compare this results, Eq. (1.30) and Eq. (1.31) with our previous calculations.<sup>28</sup> If we take the  $l=0$  term from Eq. (2.21) in Ref. 28, we can obtain

$$\tilde{p}_{l=0}(*, \mu, s|*, \mu_0) = \frac{e^{Fa(\mu - \mu_0)} \sigma - \sigma_1}{4\pi a^2 \Delta_0(\sigma)}. \quad (1.32)$$

By averaging over the initial angle and taking the surface integral over the reaction surface, we can get the global binding probability of the  $l=0$  term,

$$\tilde{p}_{l=0}(*, s|*) = \frac{\Psi(\sigma - \sigma_1)}{\Delta_0(\sigma)}. \quad (1.33)$$

The survival probability of the  $l = 0$  term can be obtained

from Eq. (2.28) in Ref. 28 as

$$\tilde{S}_{l=0}(s|*, \mu_0) = \frac{k_d \sinh(Fa) e^{-Fa\mu_0}}{Fa} \frac{\sigma + F\gamma}{(\sigma^2 - F^2) \Delta_0(\sigma)}. \quad (1.34)$$

As averaging over the initial angle, we can obtain the survival probability of the  $l = 0$  term in the Laplace domain as

$$\tilde{S}_{l=0}(s|*) = \frac{\Psi k_d (\sigma + F\gamma)}{(\sigma^2 - F^2) \Delta_0(\sigma)}. \quad (1.35)$$

Noting that  $\Psi \rightarrow 1$  and  $F\gamma \rightarrow 1/a$  when  $Fa \rightarrow 0$ , one can see that Eqs. (1.30) and (1.31) reduce to Eqs. (1.33) and (1.35), respectively when  $Fa \rightarrow 0$ .

**An Initially Separated Pair.** For an initially separated pair, the global binding probability density function,  $p(*, \tau|r_0)$  and the survival probability,  $S_{rev}(\tau|r_0)$  satisfy the following equations:

$$\frac{dp(*, \tau|r_0)}{d\tau} = k_a p(a, \tau|r_0) - (k_d + k_0) p(*, \tau|r_0), \quad (2.1)$$

$$K_{irr}(\tau|r_0) + \int_0^\tau k_a p(*, \tau'|r_0) K_{irr}(\tau - \tau'|a) d\tau' = (k_a + k_q) p(a, \tau|r_0), \quad (2.2)$$

$$S_{irr}(\tau|r_0) + \int_0^\tau k_a p(*, \tau'|r_0) S_{irr}(\tau - \tau'|a) d\tau' = S_{rev}(\tau|r_0), \quad (2.3)$$

$$p(*, \tau = 0|r_0) = 0, \quad (2.4)$$

where  $p(*, \tau|r_0) = 1 - S_{rev}(\tau|r_0)$  and  $K_{irr}(\tau|r_0) = -\partial S_{irr}(\tau|r_0) / \partial \tau - k'_0 S_{irr}(\tau|r_0)$ . By taking the Laplace transform, we get the following expressions:

$$\tilde{p}(*, s|r_0) = \frac{k_a \{1 - (s+k'_0) \tilde{S}_{irr}(s|r_0)\}}{(k_a + k_q)(s+k_d+k_0) - k_a k_d + k_a k_d (s+k'_0) \tilde{S}_{irr}(s|a)}, \quad (2.5)$$

$$\tilde{S}_{rev}(s|r_0) = \frac{\{(k_a + k_q)(s+k_d+k_0) - k_a k_d\} \tilde{S}_{irr}(s|r_0) + k_a k_d \tilde{S}_{irr}(s|a)}{(k_a + k_q)(s+k_d+k_0) - k_a k_d + k_a k_d (s+k'_0) \tilde{S}_{irr}(s|a)}. \quad (2.6)$$

It is easily shown that two equations satisfy the normalization condition, Eq. (1.8). As using Eq. (1.29),  $\tilde{p}_{l=0}(*, s|r_0)$  and  $\tilde{S}_{rev,l=0}(s|r_0)$  can be obtained from Eqs. (2.5) and (2.6) as follows:

$$\tilde{p}_{l=0}(*, s|r_0) = \frac{k_a}{(k_a + k_q) \Delta_0'(\sigma)} \left[ (1 - \Xi)(\sigma - \sigma_1) - \Psi(\sigma_1 + F\gamma) \frac{a}{r_0} e^{-\sigma(r_0 - a)} \right], \quad (2.7)$$

$$\tilde{S}_{rev,l=0}(s|r_0) = \frac{1}{(s+k'_0) \Delta_0'(\sigma)} \left[ \Omega_0 + \Omega_1 \frac{a}{r_0} e^{-\sigma(r_0 - a)} \right], \quad (2.8)$$

where

$$\Omega_0 = \Xi(\sigma - \sigma_1) \left( \sigma^2 - \sigma_2 - \frac{k_a k_d}{k_a + k_q} \right) + \Psi \frac{k_a k_d}{k_a + k_q} (\sigma + F\gamma), \quad (2.9)$$

$$\Omega_1 = \Psi(F\gamma + \sigma_1) \left( \sigma^2 - \sigma_2 - \frac{k_a k_d}{k_a + k_q} \right). \quad (2.10)$$

Now, we can compare this results, Eq. (2.7) and Eq. (2.8) with our previous results.<sup>28</sup> If we take the  $l = 0$  term from Eq. (2.23) in Ref. 28, we can get

$$\tilde{p}_{l=0}(*, \mu, s|r_0, \mu_0) = \frac{k_a}{4\pi a r_0} \frac{e^{Fa(\mu - r_0\mu_0) - \sigma(r_0 - a)}}{\Delta_0(\sigma)}. \quad (2.11)$$

As averaging over the initial angle and taking the surface integral over the reaction surface, we obtain the global probability density function of the  $l = 0$  term,

$$\tilde{p}_{l=0}(*,s|r_0) = \Xi \frac{ak_a e^{-\sigma(r_0-a)}}{r_0 \Delta_0(\sigma)}. \quad (2.12)$$

The survival probability of the  $l = 0$  term can be obtained from Eq. (2.30) in Ref. 28 as

$$\tilde{S}_{l=0}(s|r_0, \mu_0) = \frac{1}{s+k_0'} \frac{\sinh(Fa) e^{-Fr_0 \mu_0}}{Fr_0} \cdot \frac{C_0 \sigma^2 + C_1}{(\sigma^2 - F^2) \Delta_0(\sigma)} e^{-\sigma(r_0-a)}, \quad (2.13)$$

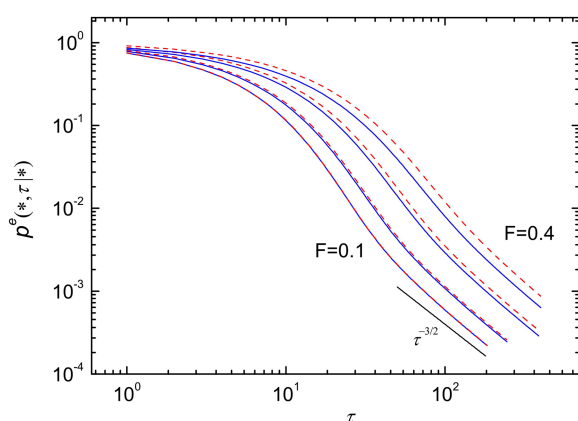
where  $C_0 = -F\gamma - \sigma_1$  and  $C_1 = -C_0 \sigma_2 - k_a k_d$ . As averaging over the initial angle, we can obtain the survival probability of the  $l = 0$  term,

$$\tilde{S}_{l=0}(s|r_0) = \frac{1}{s+k_0'} \left[ 1 - \Xi \frac{a C_0 \sigma^2 + C_1}{r_0 \Delta_0(\sigma)} e^{-\sigma(r_0-a)} \right]. \quad (2.14)$$

If  $Fa \rightarrow 0$ , then  $\Xi \rightarrow 1$ ,  $\Psi \rightarrow 1$ , and  $F\gamma \rightarrow 1/a$ . In this case, Eqs. (2.7) and (2.8) reduce to Eqs. (2.12) and (2.14), respectively.

### Numerical Result

The numerical results of the binding probability density functions and the survival probabilities are shown in Figure 1. They are calculated in the time domain by taking the inverse Laplace transform.<sup>34</sup> To compare two results of the direct calculation method and the previous calculation in Ref. 28, the binding probability density functions for the initially bound pair [Eq. (1.30) and Eq. (1.33)] are chosen. Note that the  $l = 0$  terms show the correct kinetic behavior because of their dominant contributions over all series solutions.<sup>28</sup> The dimensionless parameter values are  $a = 1.0$ ,  $k_a = 9.0$ ,  $k_d = 1.0$ ,  $k_q = 0.5$ ,  $k_0 = 0.1$ , and  $k_0' = 0.02$ . The field



**Figure 1.** The effective binding probability density functions,  $p_{l=0}^e(*, \tau | *) = p_{l=0}(*, \tau | *) e^{(F^2+k_0')\tau}$  for several values of  $F$ . The blue lines are calculated from the current direct method [Eq. (1.30)] and the red dash lines correspond to the previous results [Eq. (1.33)]. As the field strength decreases, the discrepancy between two equations decreases. The parameter values are  $a = 1.0$ ,  $k_a = 9.0$ ,  $k_d = 1.0$ ,  $k_q = 0.5$ ,  $k_0 = 0.1$ , and  $k_0' = 0.02$ . The field strength  $F$  is 0.1, 0.25, 0.35, and 0.4 from bottom to top.

strength  $F$  is changed from 0.1 to 0.4. When the field strength is small, two calculations show good agreement as expected. As the field strength increases, the discrepancy between two results increases. However, both results predict the same  $\tau^{-3/2}$  power law behavior at long times below the critical field. The critical field was given by  $F_c = \sqrt{k_0 - k_0' + k_d(k_q + 1/a)/(k_a + k_q + 1/a)} \sim 0.472$  as shown in the previous study.<sup>28</sup> Thus, the direct calculation method provides one simpler way to calculate the binding probability density functions and the survival probabilities.

### Conclusions

The direct calculation method to calculate the binding probability density functions and the survival (separation) probabilities has been generalized to the excited-state diffusion-influenced reversible reactions with quenching under an external field in three dimensions. The current method requires the irreversible survival probability function with an initial separation, which can be calculated more easily. With the confirmed normalization condition, the solutions of binding and survival probabilities for both initially bound and separated pairs are obtained in a closed form. However, the irreversible survival probability, due to the asymmetric boundary condition coming from the unidirectional external field against the spherical reaction surface, has the series solutions as in the previous study.<sup>28</sup> By the diagonal approximation, the dominantly contributing factor of the solution can be obtained. The numerical results of the present method are found to be in good agreement with those of the previous calculations and the overall qualitative behavior including the long-time asymptotic power laws is correctly predicted. The accuracy of solutions increases in the weak field or in the short reaction distance limit. It turns out that the direct method using the relation between the irreversible and reversible survival probabilities is a simple way to obtain the relevant solutions without the complicated calculation of probability density functions.<sup>28</sup> However, it should be noted that the present method neglects the detailed information such as the probability density at a local region of reaction surface, which can be useful to survey the spatial reactivity as an active site of an enzyme.<sup>5,6</sup>

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