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Effect of an external field on the reversible reaction of a neutral particle and a charged particle in three dimensions. II. Excited-state reaction

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The excited-state reversible reaction of a neutral particle and a charged particle in an external electric field is studied in three dimensions. This work extends the previous investigation for the ground-state reaction [S. Y. Reigh *et al.*, J. Chem. Phys. **129**, 234501 (2008)] to the excited-state reaction with two different lifetimes and quenching. The analytic series solutions for all the fundamental probability density functions are obtained with the help of the diagonal approximation. They are found to be in excellent agreement with the exact numerical solutions of anisotropic diffusion-reaction equations. The analytical solutions for reaction rates and survival probabilities are also obtained. We find that the long-time kinetic transition from a power-law decrease to an exponential increase can be controlled by the external field strength or excited-state decay rates or both. © 2010 American Institute of Physics. [doi:10.1063/1.3394894]

I. INTRODUCTION

One of long standing issues in diffusion-influenced reactions is the external field effect^{1–20} since it is common in a broad range of experiments.¹ For molecules with electric charges or dipole moments, the external electric field can be a useful controllable factor.^{6–14} Similarly, the external magnetic field has been a valuable tool for various molecular studies. Even for a nonpolar particle, the ubiquitous gravitational force can affect its Brownian motion and change its ultimate fate in diffusion-reaction systems.⁵ From a theoretical point of view, however, the rigorous inclusion of the external field effect significantly increases the mathematical difficulty, especially in three dimensions (3D), since it breaks down the spatial symmetry and we have to solve anisotropic diffusion-reaction equations. The previous theoretical investigations in 3D focused on the irreversible reactions including the ion pair recombination problem^{6–8} and the reaction between a neutral and an ion particle^{10–13} in the presence of an external electric field.

The recent studies for reversible effects on diffusion-influenced reactions have attracted growing interest.^{15–30} Exact analytical solutions for a variety of reversible diffusion-influenced reactions have been discovered. The ground-state solutions for the $A+B \leftrightarrow C$ type reaction^{21,22} were extended to the excited-state reactions with two different lifetimes and quenching.^{23,24} The $A+B \leftrightarrow C+D$ type reactions were solved for the ground-state and excited-state reactions.^{25,26} The trapping problem was successfully extended to the reversible case.²⁷ The effects of an external field on reversible diffusion-influenced reactions were exactly solved for various cases but only in one dimension (1D) using the mathematical isomorphism.^{5–19} The 3D analytical solutions in the

presence of a constant external field were obtained only very recently for the ground-state reversible reaction for a neutral and an ion molecule (Paper I).²⁰

An interesting kinetic transition at long times was predicted for the excited-state reactions with two different lifetimes^{28,29} and this kinetic transition behavior was confirmed experimentally for the proton transfer reactions.³⁰ On the other hand, the external field effect was found to cause a similar kinetic transition behavior.^{16–19} Since the field strength is much easier to control experimentally than the excited-state lifetimes, the transition behavior can be observed without efforts to find reactants with appropriate lifetimes.³¹ The intriguing interplay effect between the field strength and lifetimes on the long-time kinetic transition behaviors was reported in 1D.^{16,19} Therefore, the field effect on excited-state 3D reactions is of interest. In this article, we investigate the external field effect on the diffusion-influenced geminate recombination of a neutral particle and a charged particle with two different excited-state lifetimes and quenching in 3D.

This paper is organized as follows. In Sec. II, the kinetic equations of probability density functions are analytically solved and then simplified using the diagonal approximation. The analytical expressions of reaction rates and survival probabilities are obtained. In Sec. III, the long-time kinetic transition behaviors for probability density functions and survival probabilities are revealed. The irreversible association and dissociation reactions are analyzed in Sec. IV. The numerical results are discussed in Sec. V followed by concluding remarks in Sec. VI.

II. THEORY AND SOLUTION

We consider two Brownian particles under the influence of a constant external field in 3D: One is a neutral particle A and the other is an excited particle $(B^*)^q$ with a charge q . When two particles collide, they can associate with the in-

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trinsic rate constant k_a into the excited-state bound pair $(AB^*)^q$, which can dissociate reversibly into the 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, a bimolecular quenching process with the quenching rate constant k_q competes with the association reaction. Thus, the reaction mechanism can be schematically written as



The frame of reference is chosen such that the particle A is at the origin 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, making the system symmetric about the azimuthal angle in the spherical polar coordinate.

Let $\rho(r, \mu, \tau | *, \mu_0)$ be the probability density function to observe the particle $(B^*)^q$ at a distance r and an angle μ at time t for an initially bound particle $(AB^*)^q$ with an angle μ_0 . Here, $*$ denotes the bound state and $\mu = \cos \theta$ with the polar angle θ . Using similar methods to those used for an initially separated pair,^{20,32} we can derive solutions for an initially bound particle. The density function satisfies the following Debye–Smoluchowski equation:¹

$$\begin{aligned} \frac{\partial \rho(r, \mu, \tau | *, \mu_0)}{\partial \tau} = & \nabla \cdot [\nabla \rho(r, \mu, \tau | *, \mu_0) \\ & + \rho(r, \mu, \tau | *, \mu_0) \nabla W] \\ & - k'_0 \rho(r, \mu, \tau | *, \mu_0), \end{aligned} \quad (2.2)$$

where $\tau = Dt$, D is the relative diffusion constant of the unbound pair, and W is the potential energy multiplied by $\beta = 1/k_B T$ with the Boltzmann constant k_B and the temperature T . It should be noted that k'_0/D is redefined as k'_0 for simplicity and all the other rate constants (k_a , k_d , k_q , and k_0) are redefined similarly henceforth. We have $W(r, \mu) = -2k_F r$, where $k_F = F\mu$, $F = \beta|q|ED_B/(2D)$, and D_B is the diffusion constant of $(B^*)^q$. The kinetic equation for the binding probability function $\rho(*, \mu, \tau | *, \mu_0)$, which is the probability to observe $(AB^*)^q$ at an angle μ and time τ , is given by

$$\begin{aligned} \frac{\partial \rho(*, \mu, \tau | *, \mu_0)}{\partial \tau} = & k_a \rho(a, \mu, \tau | *, \mu_0) \\ & - (k_d + k_0) \rho(*, \mu, \tau | *, \mu_0). \end{aligned} \quad (2.3)$$

The generalized anisotropic boundary condition at the reaction distance a and the normalized initial condition can be written as

$$\begin{aligned} \left. \frac{\partial \rho(r, \mu, \tau | *, \mu_0)}{\partial r} \right|_{r=a} = & (k_a + k_d + 2k_F) \rho(a, \mu, \tau | *, \mu_0) \\ & - k_d \rho(*, \mu, \tau | *, \mu_0), \end{aligned} \quad (2.4)$$

$$\rho(*, \mu, 0 | *, \mu_0) = \frac{1}{2\pi a^2} \delta(\mu - \mu_0). \quad (2.5)$$

Note that $\rho(r, \mu, 0 | *, \mu_0) = 0$ by definition.

The following two transformations:

$$\rho(r, \mu, \tau | *, \mu_0) = \frac{1}{2\pi} e^{1/2[W(a, \mu_0) - W(r, \mu)]} h(r, \mu, \tau | *, \mu_0), \quad (2.6)$$

$$\rho(*, \mu, \tau | *, \mu_0) = \frac{1}{2\pi} e^{1/2[W(a, \mu_0) - W(a, \mu)]} h(*, \mu, \tau | *, \mu_0) \quad (2.7)$$

are useful to make Eqs. (2.2)–(2.5) more tractable equations as

$$\begin{aligned} \frac{\partial h(r, \mu, \tau | *, \mu_0)}{\partial \tau} = & \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - (F^2 + k'_0) \right] h(r, \mu, \tau | *, \mu_0) \\ & + \frac{1}{r^2} \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial h(r, \mu, \tau | *, \mu_0)}{\partial \mu} \right], \end{aligned} \quad (2.8)$$

$$\begin{aligned} \frac{\partial h(*, \mu, \tau | *, \mu_0)}{\partial \tau} = & k_a h(a, \mu, \tau | *, \mu_0) \\ & - (k_d + k_0) h(*, \mu, \tau | *, \mu_0), \end{aligned} \quad (2.9)$$

$$\begin{aligned} \left. \frac{\partial h(r, \mu, \tau | *, \mu_0)}{\partial r} \right|_{r=a} = & (F\mu + k_a + k_q) h(a, \mu, \tau | *, \mu_0) \\ & - k_d h(*, \mu, \tau | *, \mu_0), \end{aligned} \quad (2.10)$$

$$h(*, \mu, 0 | *, \mu_0) = \frac{1}{a^2} \delta(\mu - \mu_0). \quad (2.11)$$

Then, we can separate angular and radial variables of $h(r, \mu, \tau | *, \mu_0)$ using

$$h(r, \mu, \tau | *, \mu_0) = \sum_{l=0}^{\infty} A_l(\mu_0) P_l(\mu) R_l(r, \tau | *), \quad (2.12)$$

where the angular Legendre function $P_l(\mu)$ and the radial function $R_l(r, \tau | *)$ satisfy the following respective equations:

$$\frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial P_l(\mu)}{\partial \mu} \right] + l(l+1) P_l(\mu) = 0, \quad (2.13)$$

$$\begin{aligned} \frac{\partial R_l(r, \tau | *)}{\partial \tau} = & \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \left(F^2 + k'_0 + \frac{l(l+1)}{r^2} \right) \right] \\ & \times R_l(r, \tau | *). \end{aligned} \quad (2.14)$$

The constant $A_l(\mu_0)$ is determined by the initial condition.

Since the delta function can be expanded in terms of the Legendre polynomials as $\delta(\mu - \mu_0) = \sum_{l=0}^{\infty} A_l(\mu_0) P_l(\mu)$, we have $A_l(\mu_0) = (2l+1)P_l(\mu_0)/2$.

In the Laplace-transformed $[\tilde{f}(s) = \int_0^\infty f(\tau) e^{-s\tau} d\tau]$ space, Eq. (2.14) with the initial condition $R_l(*, 0|*) = 1/a^2$ can be written as

$$\frac{\partial^2 \tilde{R}_l}{\partial r^2} + \frac{2}{r} \frac{\partial \tilde{R}_l}{\partial r} - \left(s + F^2 + k_0' + \frac{l(l+1)}{r^2} \right) \tilde{R}_l = 0. \quad (2.15)$$

Two linearly independent solutions of this homogenous differential equation can be expressed by the modified spherical Bessel functions of fractional order: $y_{1l}(r, s) = \{\pi/(2\sigma r)\}^{1/2} I_{l+1/2}(\sigma r)$ and $y_{2l}(r, s) = \{\pi/(2\sigma r)\}^{1/2} K_{l+1/2}(\sigma r)$, where $\sigma = (s + F^2 + k_0')^{1/2}$.³³ Considering the outer boundary condition, we have

$$\tilde{R}_l(r, s|*) = \alpha_l(s) y_{2l}(r, s), \quad (2.16)$$

where $\alpha_l(s)$ is to be determined by the inner boundary condition.

By eliminating $\tilde{h}(*, \mu, s|*, \mu_0)$ from Eqs. (2.9) and (2.10), we obtain

$$\left. \frac{\partial \tilde{h}(r, \mu, s|*, \mu_0)}{\partial r} \right|_{r=a} = \{B(s) + F\mu\} \tilde{h}(a, \mu, s|*, \mu_0) - H(s) \delta(\mu - \mu_0), \quad (2.17)$$

where $B(s) = k_q + k_a - k_d k_d / (s + k_d + k_0)$ and $H(s) = k_d / \{a^2(s + k_d + k_0)\}$. By re-expanding the right hand side of Eq. (2.17) in terms of Legendre polynomials such as Eq. (2.12) with the recurrence relation $(2l+1)P_l P_l = (l+1)P_{l+1} + lP_{l-1}$, we obtain the following infinite matrix formula to find $\alpha_l(s)$:

$$\begin{pmatrix} D_0 & E_{20} & & & \\ E_{11} & D_1 & E_{21} & & \\ & E_{12} & D_2 & E_{22} & \\ & & & \ddots & \\ & & E_{1l} & D_l & E_{2l} \\ & & & & \ddots \end{pmatrix} \begin{pmatrix} \alpha_0 \\ \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_l \\ \vdots \end{pmatrix} = \begin{pmatrix} H \\ H \\ H \\ \vdots \\ H \\ \vdots \end{pmatrix}, \quad (2.18)$$

where the elements are defined as $D_l(s) = B(s) y_{2l}(a, s) - y_{2l}'(a, s)$,

$$E_{1l}(\mu_0, s) = F \frac{l}{2l+1} \frac{P_{l-1}(\mu_0)}{P_l(\mu_0)} y_{2l-1}(a, s),$$

$$E_{2l}(\mu_0, s) = F \frac{l+1}{2l+1} \frac{P_{l+1}(\mu_0)}{P_l(\mu_0)} y_{2l+1}(a, s),$$

and y_{2l}' is the first derivative with respect to r . If we assume that E_{il}/D_l ($i=1, 2$) is small enough, we obtain $\alpha_l(s)$ as

$$\alpha_l(s) \cong \frac{H(s)}{B(s) y_{2l}(a, s) - y_{2l}'(a, s)} + \mathcal{O}\left(\frac{E_{il}}{D_l}\right). \quad (2.19)$$

In the small F limit, we get $E_{il}/D_l \sim \text{constant} \times F + \mathcal{O}(F^3)$ and $H/D_l \sim \text{constant} + \mathcal{O}(F^2)$. Therefore, we can reduce the tridiagonal matrix for the initially bound state in Eq. (2.18)

to the diagonal one in the small F limit. Under this diagonal approximation, we can obtain the probability density functions in the Laplace domain as

$$\begin{aligned} \tilde{\rho}(r, \mu, s|*, \mu_0) &= \frac{1}{4\pi a^2} e^{F(r\mu - a\mu_0)} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) P_l(\mu) \\ &\times \frac{k_d}{(s + k_d + k_0)} \frac{y_{2l}(r, s)}{B(s) y_{2l}(a, s) - y_{2l}'(a, s)}, \end{aligned} \quad (2.20)$$

$$\begin{aligned} \tilde{\rho}(*, \mu, s|*, \mu_0) &= \frac{1}{4\pi a^2} e^{Fa(\mu - \mu_0)} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) P_l(\mu) \\ &\times \frac{1}{(s + k_d + k_0)} \frac{(k_q + k_a) y_{2l}(a, s) - y_{2l}'(a, s)}{B(s) y_{2l}(a, s) - y_{2l}'(a, s)}. \end{aligned} \quad (2.21)$$

The probability density functions for the initially unbound state separated by r_0 can be obtained similarly. Following the procedure of our previous work,²⁰ we can obtain

$$\begin{aligned} \tilde{\rho}(r, \mu, s|r_0, \mu_0) &= \frac{1}{4\pi} e^{F(r\mu - r_0\mu_0)} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) P_l(\mu) \\ &\times \frac{\bar{y}_{1l}(\min(r, r_0), s) y_{2l}(\max(r, r_0), s)}{\pi/(2\sigma)}, \end{aligned} \quad (2.22)$$

$$\begin{aligned} \tilde{\rho}(*, \mu, s|r_0, \mu_0) &= \frac{1}{4\pi a^2} e^{Fa(\mu - r_0\mu_0)} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) P_l(\mu) \\ &\times \frac{k_a}{s + k_d + k_0} \frac{y_{2l}(r_0, s)}{B(s) y_{2l}(a, s) - y_{2l}'(a, s)}, \end{aligned} \quad (2.23)$$

where $\bar{y}_{1l}(r, s) = y_{1l}(r, s) - \alpha_l(s) y_{2l}(r, s)$. From the diagonal approximation, α_l is given by $\alpha_l \cong \{B(s) y_{1l}(a, s) - y_{1l}'(a, s)\} / \{B(s) y_{2l}(a, s) - y_{2l}'(a, s)\}$. Comparison of Eq. (2.20) with Eq. (2.23) leads to the detailed balance condition

$$k_a \rho(r, \mu, \tau|*, \mu_0) e^{2Fa\mu_0} = k_d \rho(*, \mu_0, \tau|r, \mu) e^{2Fr\mu}. \quad (2.24)$$

By integrating the kinetic equations and using the Gauss's theorem, we obtain the following equation irrespective of the initial condition:

$$-\frac{dS(\tau)}{d\tau} = - \int_{\Gamma=\Sigma} [\nabla \rho + \rho \nabla W] d\Gamma + k_0' S(\tau), \quad (2.25)$$

where Σ is the reaction surface and $S(\tau)$ is the total survival probability of $(B^*)^q$. Since the reaction rate is defined as the surface integral of the flux through the reaction boundary, we obtain the useful relation between the survival probability and the rate of reaction as

$$-\frac{dS(\tau)}{d\tau} = K(\tau) + k'_0 S(\tau). \quad (2.26)$$

This equation means that the survival probability changes due to two contributions of the association-dissociation reactions between A and $(B^*)^q$ and the unimolecular decay rate.

Using the above diagonal approximation, the reaction rate and the survival probability for the initially bound pair are easily derived as

$$\begin{aligned} \tilde{K}(s|*, \mu_0) &= e^{-F a \mu_0} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) \frac{k_d}{s + k_d + k_0} \\ &\quad \times \frac{y_{1l}(a, -k'_0) y'_{2l}(a, s) - y_{2l}(a, s) y'_{1l}(a, -k'_0)}{B(s) y_{2l}(a, s) - y'_{2l}(a, s)}, \end{aligned} \quad (2.27)$$

$$\tilde{S}(s|*, \mu_0) = -\frac{\tilde{K}(s|*, \mu_0)}{s + k'_0}. \quad (2.28)$$

For the initially unbound case, we have

$$\begin{aligned} \tilde{K}(s|r_0, \mu_0) &= e^{-F r_0 \mu_0} \sum_{l=0}^{\infty} (2l+1) P_l(\mu_0) y_{2l}(r_0, s) \\ &\quad \times \frac{B(s) y_{1l}(a, -k'_0) - y'_{1l}(a, -k'_0)}{B(s) y_{2l}(a, s) - y'_{2l}(a, s)}, \end{aligned} \quad (2.29)$$

$$\tilde{S}(s|r_0, \mu_0) = \frac{1 - \tilde{K}(s|r_0, \mu_0)}{s + k'_0}. \quad (2.30)$$

Thus, one can easily check that the following normalization condition holds:²⁴

$$(s + k'_0) \tilde{S}(s) + (s + k_0) \tilde{p}(*, s) + k_q \tilde{p}(a, s) = 1, \quad (2.31)$$

where $\tilde{p}(s) = \int_{\Sigma} \tilde{p}(s) d\Gamma$. It should be noted that the survival probabilities can be alternatively derived from the kinetic equations without the detail calculations of the probability density functions.^{20,34,35}

III. ASYMPTOTIC KINETIC TRANSITION BEHAVIORS

When excited molecules have different lifetimes or the system is affected by the external field, the kinetic transitions at long times have been predicted for various reversible diffusion-influenced reactions.²³⁻³⁰ In the present system, we have to consider both different-lifetime and external field effects that affect the pattern of the long-time kinetic transition behaviors.

The diagonal approximation, which is valid in the weak field limit, allows us to obtain analytical solutions in the form of series expansions in the Laplace domain as shown above. We find that the vast majority of the contribution to the long-time dynamics comes from the lowest-order ($l=0$) term in the series expansions, which can be analytically inverted to give time-domain results. For the initially unbound pair, we have

$$\begin{aligned} \rho_{l=0}^e(r, \mu, \tau|r_0, \mu_0) &= \frac{1}{4\pi r r_0} e^{F(r\mu - r_0\mu_0)} \left\{ \frac{1}{\sqrt{4\pi\tau}} [e^{-(r-r_0)^2/4\tau} + e^{-(r+r_0-2a)^2/4\tau}] \right. \\ &\quad \left. + \sum_{i=1}^3 \frac{\sigma_i(\sigma_j + \sigma_i)(\sigma_k + \sigma_i)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \Phi_i(r + r_0 - 2a, \tau) \right\}, \end{aligned} \quad (3.1)$$

where three roots σ_i , σ_j , and σ_k ($i \neq j \neq k=1, 2$, or 3) satisfy the following relations:

$$\kappa_1 = \sigma_1 + \sigma_2 + \sigma_3 = -(k_a + k_q + 1/a), \quad (3.2)$$

$$\kappa_2 = \sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1 = k_d - F^2 + k_0 - k'_0, \quad (3.3)$$

$$\kappa_3 = \sigma_1 \sigma_2 \sigma_3 = \kappa_1 \kappa_2 + k_a k_d, \quad (3.4)$$

and

$$\Phi_i(r, \tau) = \exp(\sigma_i^2 \tau - \sigma_i r) \operatorname{erfc}\left(\frac{r}{\sqrt{4\tau}} - \sigma_i \sqrt{\tau}\right), \quad (3.5)$$

with the complementary error function $\operatorname{erfc}(x)$. Here, we have defined the *effective* Green function as $\rho^e = \rho e^{(F^2 + k'_0)\tau}$. Then, the other probability density functions for the $l=0$ terms can be obtained as follows:

$$\begin{aligned} \rho_{l=0}^e(*, \mu, \tau|r_0, \mu_0) &= \frac{k_a}{4\pi a r_0} e^{F(a\mu - r_0\mu_0)} \\ &\quad \times \sum_{i=1}^3 \frac{\sigma_i}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \Phi_i(r_0 - a, \tau), \end{aligned} \quad (3.6)$$

$$\begin{aligned} \rho_{l=0}^e(*, \mu, \tau|*, \mu_0) &= -\frac{1}{4\pi a^2} e^{F a(\mu - \mu_0)} \\ &\quad \times \sum_{i=1}^3 \frac{\sigma_i(\sigma_j + \sigma_k)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \Phi_i(0, \tau), \end{aligned} \quad (3.7)$$

and $\rho_{l=0}^e(r, \mu, \tau|*, \mu_0)$ can be readily obtained from the detailed balanced condition Eq. (2.24).

The long-time behaviors of effective probability density functions depend on $\Phi_i(r, \tau)$ as previously analyzed in the time domain.^{15,23} We can predict the long-time behaviors of probability functions straightforwardly in the Laplace domain without detailed analysis of three roots σ_i .^{36,37} In this way, we find that the long-time behaviors depend on the sign of κ_3 .

When $\kappa_3 < 0$, the effective probability density functions decay as $\tau^{-3/2}$ at long times as

$$\begin{aligned} \rho_{l=0}^e(r, \mu, \tau|r_0, \mu_0) &\sim \frac{e^{F(r\mu - r_0\mu_0)}}{r r_0 (4\pi\tau)^{3/2}} \left[r r_0 + a^2 + \left(\frac{\kappa_2}{\kappa_3}\right)^2 \right. \\ &\quad \left. - (r + r_0 - 2a) \left(a + \frac{\kappa_2}{\kappa_3}\right) \right], \end{aligned} \quad (3.8)$$

$$\rho_{l=0}^e(*, \mu, \tau | r_0, \mu_0) \sim \frac{k_a e^{F(a\mu - r_0\mu_0)}}{ar_0(4\pi\tau)^{3/2}} \frac{1}{\kappa_3} \left[\frac{\kappa_2}{\kappa_3} - (r_0 - a) \right], \quad (3.9)$$

$$\rho_{l=0}^e(*, \mu, \tau | *, \mu_0) \sim \frac{e^{Fa(\mu - \mu_0)}}{a^2(4\pi\tau)^{3/2}} \frac{k_a k_d}{\kappa_3^2}. \quad (3.10)$$

When $\kappa_3=0$ or

$$F^2 + k_0' = k_0 + k_d(k_q + 1/a)/(k_a + k_q + 1/a), \quad (3.11)$$

one root vanishes and the transition behavior of $\tau^{-1/2}$ decrease is observed as

$$\rho_{l=0}^e(r, \mu, \tau | r_0, \mu_0) \sim \frac{1}{4\pi r r_0 \sqrt{\pi\tau}} e^{F(r\mu - r_0\mu_0)}, \quad (3.12)$$

$$\rho_{l=0}^e(*, \mu, \tau | r_0, \mu_0) \sim \frac{k_a}{4\pi a r_0 \kappa_2 \sqrt{\pi\tau}} e^{F(a\mu - r_0\mu_0)}, \quad (3.13)$$

$$\rho_{l=0}^e(*, \mu, \tau | *, \mu_0) \sim -\frac{1}{4\pi a^2 \sqrt{\pi\tau} \kappa_2} \frac{\kappa_1}{\kappa_2} e^{Fa(\mu - \mu_0)}. \quad (3.14)$$

When $\kappa_3 > 0$, the long-time effective density functions increase exponentially as

$$\rho_{l=0}^e(r, \mu, \tau | r_0, \mu_0) \sim \frac{1}{2\pi r r_0} \frac{\sigma_i(\sigma_j + \sigma_i)(\sigma_k + \sigma_i)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \times e^{\sigma_i^2 \tau - \sigma_i(r + r_0 - 2a) + F(r\mu - r_0\mu_0)}, \quad (3.15)$$

$$\rho_{l=0}^e(*, \mu, \tau | r_0, \mu_0) \sim \frac{k_a}{2\pi a r_0} \frac{\sigma_i}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \times e^{\sigma_i^2 \tau - \sigma_i(r_0 - a) + F(a\mu - r_0\mu_0)}, \quad (3.16)$$

$$\rho_{l=0}^e(*, \mu, \tau | *, \mu_0) \sim -\frac{1}{2\pi a^2} \frac{\sigma_i(\sigma_j + \sigma_k)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \times e^{\sigma_i^2 \tau + Fa(\mu - \mu_0)}, \quad (3.17)$$

where σ_i is the positive root.

We can change the fate of effective probability density functions by controlling the field strength or the rate constants. In a usual experiment, we can control the field strength more easily than the rate constants. The critical field F_c to determine kinetic transition behaviors is given by $F_c = \sqrt{k_0 - k_0' + k_d(k_q + 1/a)/(k_a + k_q + 1/a)}$ from Eq. (3.11). The long-time effective density functions decay as $\tau^{-3/2}$ when $F < F_c$ and increase exponentially when $F > F_c$. When $F = F_c$, they decay as $\tau^{-1/2}$.

On the other hand, the effective survival probabilities always increase exponentially. The lowest-order terms of the effective survival probabilities in the time domain are given by

$$S_{l=0}^e(\tau | r_0, \mu_0) = e^{F^2 \tau} - \frac{\sinh(Fa) e^{-Fr_0\mu_0}}{Fr_0} \times \sum_{i=1}^5 \frac{\sigma_i(C_0\sigma_i^2 + C_1)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)(\sigma_l - \sigma_i)(\sigma_m - \sigma_i)} \times \Phi_i(r_0 - a, \tau), \quad (3.18)$$

$$S_{l=0}^e(\tau | *, \mu_0) = \frac{k_d \sinh(Fa) e^{-Fa\mu_0}}{Fa} \times \sum_{i=1}^5 \frac{\sigma_i(\sigma_i + F\gamma)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)(\sigma_l - \sigma_i)(\sigma_m - \sigma_i)} \times \Phi_i(0, \tau), \quad (3.19)$$

where $C_0 = -(\kappa_1 + F\gamma)$, $C_1 = C_0\kappa_2 - k_d k_d$, and $\gamma = \coth(Fa)$. Here, we have five roots; the same three roots as in Eqs. (3.2)–(3.4) and additional two roots of $\sigma_4 = -F$ and $\sigma_5 = F$ ($i \neq j \neq k \neq l \neq m = 1, 2, 3, 4, \text{ or } 5$). At long times, the survival probabilities are given by

$$S_{l=0}^e(\tau | r_0, \mu_0) \sim \left[1 + \frac{(1 - e^{2Fa})}{2Fr_0} \frac{C_0(F^2 + \kappa_2) - k_d k_d}{(F - \kappa_1)(F^2 + \kappa_2) - k_d k_d} e^{-Fr_0(\mu_0 + 1)} \right] \times e^{F^2 \tau}, \quad (3.20)$$

$$S_{l=0}^e(\tau | *, \mu_0) \sim \frac{1}{a} \frac{k_d}{(F - \kappa_1)(F^2 + \kappa_2) - k_d k_d} e^{F^2 \tau - Fa(\mu_0 - 1)}. \quad (3.21)$$

It should be noted that, when $k_0' = 0$, $S_{l=0}(\infty)$ converges to certain values.

IV. IRREVERSIBLE CASES

An interesting special limit of the above general results is the irreversible case since we can observe different behaviors from those in the reversible case. In this section, we discuss the irreversible association ($k_d = 0$) and dissociation ($k_a = 0$) cases in detail. For both irreversible cases, we can simplify probability functions and survival probabilities using the fact that $\kappa_3 = \kappa_1 \kappa_2$ and three roots are given by $\sigma_1 = \kappa_1$, $\sigma_2 = \sqrt{-\kappa_2}$, and $\sigma_3 = -\sqrt{-\kappa_2}$.

Since $\sigma_2 + \sigma_3 = 0$, Eq. (3.1) can be simplified to

$$\rho_{l=0}^e(r, \mu, \tau | r_0, \mu_0) = \frac{1}{4\pi r r_0} e^{F(r\mu - r_0\mu_0)} \left\{ \frac{1}{\sqrt{4\pi\tau}} [e^{-(r - r_0)^2/4\tau} + e^{-(r + r_0 - 2a)^2/4\tau}] + \kappa_1 \Phi_1(r + r_0 - 2a, \tau) \right\}, \quad (4.1)$$

and this function shows a $\tau^{-3/2}$ power-law decay behavior at long times as

$$\rho_{l=0}^e(r, \mu, \tau | r_0, \mu_0) \sim \frac{(r-a+1/\kappa_1)(r_0-a+1/\kappa_1)}{rr_0(4\pi\tau)^{3/2}}. \quad (4.2)$$

On the other hand, the long-time behavior of the effective binding probability function $\rho_{l=0}^e(*, \mu, \tau | r_0, \mu_0)$, which is given by Eq. (3.6) but with three roots in the irreversible case, depends on the sign of κ_2 considering that $\kappa_3 = \kappa_1\kappa_2$ and $\kappa_1 < 0$. When $\kappa_2 > 0$, it shows a power-law decay behavior of $\tau^{-3/2}$ and when $\kappa_2 < 0$, it increases exponentially. When $\kappa_2 = 0$, two roots vanish unlike the reversible case and it simplifies to

$$\rho_{l=0}^e(*, \mu, \tau | r_0, \mu_0) = -\frac{k_a e^{F(a\mu - r_0\mu_0)}}{4\pi a r_0 \kappa_1} \times \left[\operatorname{erfc}\left(\frac{r_0 - a}{\sqrt{4\tau}}\right) - \Phi_1(r_0 - a, \tau) \right], \quad (4.3)$$

which converges to a constant of $k_a e^{F(a\mu - r_0\mu_0)} / (-4\pi a r_0 \kappa_1)$. Note that this long-time behavior is contrasted with a $\tau^{-1/2}$ power-law behavior in the reversible case. One can confirm that similar results can be obtained for the function $\rho_{l=0}^e(r, \mu, \tau | *, \mu_0)$ using the detailed balance condition Eq. (2.24).

The effective binding probability $\rho^e(*, \mu, \tau | *, \mu_0)$ can be easily calculated from Eq. (2.21) as

$$\rho^e(*, \mu, \tau | *, \mu_0) = \frac{1}{2\pi a^2} \delta(\mu - \mu_0) e^{-\kappa_2 \tau}. \quad (4.4)$$

The global binding probability function is given by averaging over the initial angle μ_0 and taking the surface integral over the reaction surface Σ as $p^e(*, \tau | *) = e^{-\kappa_2 \tau}$.

The effective survival probability Eq. (3.18) in the irreversible limit can be simplified to

$$S_{l=0}^e(\tau | r_0, \mu_0) = e^{F^2 \tau} - \frac{C_0 e^{-F r_0 \mu_0} \sinh(Fa)}{F r_0} \sum_{i=1}^3 \frac{\sigma_i \Phi_i(r_0 - a, \tau)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)}, \quad (4.5)$$

where $\sigma_1 = \kappa_1$, $\sigma_2 = -F$, and $\sigma_3 = F$. The asymptotic behavior shows an exponential increase

$$S_{l=0}^e(\tau | r_0, \mu_0) \sim e^{F^2 \tau} \left[1 - \frac{C_0 (e^{2Fa} - 1) e^{-F r_0 (\mu_0 + 1)}}{2F r_0 (F - \kappa_1)} \right]. \quad (4.6)$$

One can obtain the expressions of $S_{l=0}^e(\tau | *, \mu_0)$ in the irreversible limit from Eqs. (3.19) and (3.21). Therefore, the effective irreversible survival probabilities always increase exponentially such as the reversible ones.

From Eq. (4.6), one can obtain a generalized field-free version of the irreversible escape probability, $S_{l=0}(\tau | r_0) \sim [1 + (a/r_0)\{(k_a + k_q)/\kappa_1\}] e^{-k_0' \tau}$, which reduces to the well-known result of $S_{l=0}(\infty | r_0) = 1 - (a/r_0)\{k_a/(k_a + 1/a)\}$ in the ground-state limit. This corroborates the fact that the $l=0$ term is dominant at long times. Note that, in the absorbing boundary condition limit ($k_a \rightarrow \infty$ and $k_d = 0$), we can derive

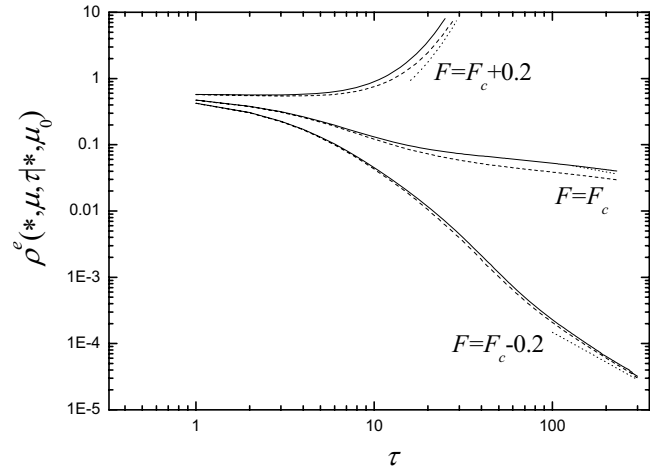


FIG. 1. The field effect: the time dependence of the effective probability density function, $\rho(*, \mu, \tau | *, \mu_0) e^{(F^2 + k_0')\tau}$ for several values of F . It shows the usual $\tau^{-3/2} \rightarrow \tau^{-1/2} \rightarrow$ exponential transition behavior as F is increased. The solid lines correspond to the numerical calculations with off-diagonal terms up to ten terms in the series sum. The dashed lines correspond to the numerical inversion of the diagonal approximation [Eq. (2.21)] and the dotted lines to the asymptotic limits for the $l=0$ term [Eqs. (3.10), (3.14), and (3.17)]. The parameter values are $k_a = 9.0$, $k_d = 1.0$, $a = 1.0$, $\mu_0 = -0.5$, $\mu = -0.5$, $k_q = 0.5$, $k_0 = 0.1$, and $k_0' = 0.1$. The critical field is given by $F_c = \sqrt{k_0 - k_0' + k_d(k_q + 1/a)} / (k_a + k_q + 1/a) = 0.3780$.

$\lim_{\tau \rightarrow \infty} [S(\tau | r_0, \mu_0) e^{k_0' \tau}] = S_g(\infty | r_0, \mu_0)$ from Eq. (2.30), where the ground-state escape probability $S_g(\infty)$ was obtained in Paper I [Eq. (5.6)].

V. NUMERICAL RESULTS

Numerically exact results can be obtained by solving the infinite matrix equation in Eq. (2.18). After the matrix size is chosen as small as possible by checking the convergence, we take the inversion of the matrix and perform the inverse Laplace transformation.³⁸ The numerical results using the diagonal approximation are obtained by numerically inverting analytic equations in Sec. II. We verify numerically that the $l=0$ term is the dominant contribution to the long-time behavior and the higher-order terms usually affect the short-time region.²⁰ Long-time results from the $l=0$ term contribution are compared to full numerical solutions.

The time dependence of the effective probability density function for the initially bound state, $\rho^e(*, \mu, \tau | *, \mu_0)$ with respect to the field strength F is shown in Fig. 1. The dimensionless parameter values are $k_a = 9.0$, $k_d = 1.0$, $a = 1.0$, $\mu_0 = -0.5$, $\mu = -0.5$, $k_q = 0.5$, $k_0 = 0.1$, and $k_0' = 0.1$. For these parameter values, the matrix of Eq. (2.18) converges so rapidly that it is enough to use 10×10 matrix and the first ten terms in the series expansions in Eq. (2.12). The solid lines show the exact numerical results with the off-diagonal terms in the matrix, the dashed lines show the diagonal approximation results. The diagonal approximation is found to produce the underestimated but qualitatively correct behaviors. Indeed, the discrepancy resulting from the diagonal approximation increases as the field strength increases. The dotted lines show the corresponding asymptotic behaviors for the $l=0$ terms which are shown to be the dominant contribution in the long time limit. One can see clearly that the kinetic tran-

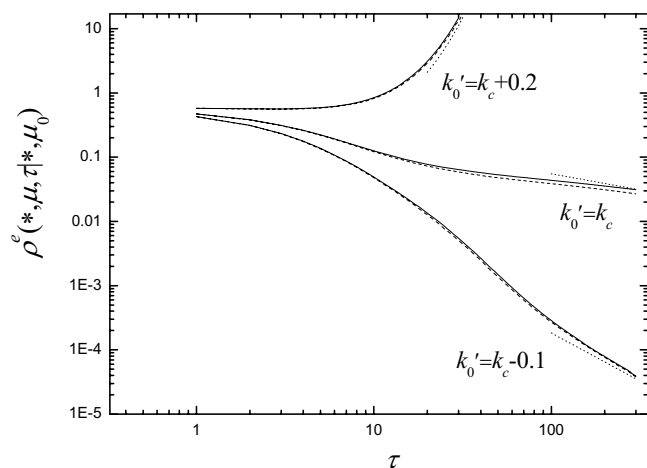


FIG. 2. The lifetime effect: the time dependence of the effective probability density function, $\rho^e(*, \mu, \tau | *, \mu_0)e^{(F^2+k'_0)\tau}$ for several values of k'_0 . It shows the usual $\tau^{-3/2} \rightarrow \tau^{-1/2} \rightarrow$ exponential transition behavior as k'_0 is increased. The solid lines correspond to the numerical calculations with off-diagonal terms up to ten terms in the series sum. The dashed lines correspond to the numerical inversion of the diagonal approximation [Eq. (2.21)] and the dotted lines to the asymptotic limits for the $l=0$ term [Eqs. (3.10), (3.14), and (3.17)]. The parameter values are $k_a=9.0$, $k_d=1.0$, $a=1.0$, $\mu_0=-0.5$, $\mu=-0.5$, $k_q=0.5$, $k_0=0.1$, and $F=0.1$. The critical rate is given by $k_c=k_0 - F^2 + k_d(k_q + 1/a)/(k_a + k_q + 1/a) = 0.2329$.

sition behavior appears from a $\tau^{-3/2}$ power law ($F < F_c$) to an exponentially increasing behavior ($F > F_c$) via a $\tau^{-1/2}$ power law at the transition region ($F = F_c$).

The time dependence of the effective probability density function, $\rho^e(*, \mu, \tau | *, \mu_0)$ with respect to the unimolecular decay rate constant k'_0 is shown in Fig. 2. The parameter values are $k_a=9.0$, $k_d=1.0$, $a=1.0$, $\mu_0=-0.5$, $\mu=-0.5$, $k_q=0.5$, $k_0=0.1$, and $F=0.1$. For these parameter values, the matrix of Eq. (2.18) also rapidly converges. The solid lines, the dashed lines, and the dotted lines correspond to the exact results, results from the diagonal approximation, and the long-time asymptotic results from the $l=0$ term, respectively, as in Fig. 1. The figure shows that the diagonal approximation again produces the underestimated but qualitatively correct behaviors in the small field strength. The kinetic transition behavior appears from a $\tau^{-3/2}$ power law to an exponentially increasing behavior via a $\tau^{-1/2}$ power law at the transition region.

VI. CONCLUSIONS

The ground-state reversible reaction of a neutral and a charged particle with a constant external electric field in 3D is generalized to the excited-state reaction with two different lifetimes and quenching. The anisotropic diffusion-reaction equations of the probability density functions are solved to provide an efficient method for the evaluation of numerically exact results. With the help of the diagonal approximation, which is shown to be quite accurate, the infinite series solutions for the probability density functions, the rate of reactions, and the survival probabilities are analytically obtained.

The usefulness of the present solutions is beyond the theoretical significance that the previous ground-state solutions are straightforwardly generalized. The generalization to the excited-state reaction greatly increases the applicability

to various experimental conditions. For instance, the present results can be directly applied to investigate the field effect on Michaelis–Menten enzyme kinetics, where the reaction mechanism is given by $E + S \rightleftharpoons ES \rightarrow E + P$.^{39–41} For the case where the reaction mechanism has more complicated unimolecular conversion steps than Eqs. (2.1c) and (2.1d), we can utilize the present results with slight modifications.

By analyzing the first term solutions, we find that the effective probability density functions showed the transition from a $\tau^{-3/2}$ power law to an exponentially increasing behavior through a $\tau^{-1/2}$ power law in the transition region but the effective survival probabilities did not show the transition but exponentially increasing behavior. The present kinetic transition behaviors are different from those in 1D mainly because we treat an anisotropic field in 3D. The amusing similarities among diffusion-reaction systems of ground- or excited-state reactions in the presence or absence of the external field in 1D or 3D are discussed in the Appendix. We also find that, in the irreversible limit, we can observe a different kinetic transition behavior such as $\tau^{-3/2} \rightarrow$ constant $\rightarrow$ exponential.

The kinetic transition is affected by both the strength of the external field and the lifetime difference between two excited states. Usually, the field strength is much easier to control experimentally than the excited-state lifetimes. The kinetic transition was experimentally verified in the excited-state proton transfer,^{30,31} but for this purpose dyes with short anion lifetimes had to be searched for. We expect that the present analysis on the external field effect makes experimental verifications for the kinetic transition in proton transfer reactions much easier.

When the concentration of reactants is very high, the competition effect that we neglect here is large and many-body approaches are needed. However, the present results can be used to devise efficient Brownian dynamics for accurate numerical results.^{42–46} When quantum mechanical effects are non-negligible, we can apply the quantum correction methods^{47–50} to classical data from efficient Brownian dynamics simulations.

ACKNOWLEDGMENTS

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APPENDIX: SIMILARITIES IN VARIOUS DIFFUSION-REACTION SYSTEMS

A variety of kinetic transition behaviors for the diffusion-influenced reversible reactions have been revealed for the past decade.^{15,16,20,23–29} In this appendix, we discuss amusing similarities in these kinetic transitions for the present results (3D_ESF), the ground-state results with an external field in 3D (3D_GSF),²⁰ the ground (1D_GSF) (Ref. 15) and excited-state results in 1D (1D_ESF),¹⁶ and the field-free results in 1D (1D_ES) (Ref. 24) and 3D (3D_ES).²³ The effective probability density functions can be defined in our notations as follows:

$$\rho_{3D_ESF}^e(r, \tau|r_0) = 4\pi r r_0 e^{-F(r\mu - r_0\mu_0) + (F^2 + k_0')\tau} \rho_{l=0}(r, \mu, \tau|r_0, \mu_0), \quad (A1)$$

$$\rho_{3D_GSF}^e(r, \tau|r_0) = 4\pi r r_0 e^{-F(r\mu - r_0\mu_0) + F^2\tau} \rho_{l=0}(r, \mu, \tau|r_0, \mu_0), \quad (A2)$$

$$\rho_{3D_ES}^e(r, \tau|r_0) = 4\pi r r_0 e^{k_0'\tau} \rho(r, \tau|r_0), \quad (A3)$$

$$\rho_{1D_ES}^e(r, \tau|r_0) = e^{k_0'\tau} \rho(r, \tau|r_0), \quad (A4)$$

$$\rho_{1D_GSF}^e(r, \tau|r_0) = e^{F(r-r_0) + F^2\tau} \rho(r, \tau|r_0), \quad (A5)$$

$$\rho_{1D_ESF}^e(r, \tau|r_0) = e^{F(r-r_0) + (F^2 + k_0')\tau} \rho(r, \tau|r_0). \quad (A6)$$

For the probability functions with the bound state, r or r_0 in the prefactor of $\rho(r, \tau|r_0)$ is replaced by the reaction distance a . The $l=0$ terms in Eqs. (A1) and (A2) are chosen since it gives the dominant contribution to the kinetic transition behaviors. The probability density functions including Eqs. (A1)–(A6) can be expressed by the same formulas, in our notation, as

$$\rho^e(r, \tau|r_0) = f_{\text{ref}}(r, \tau|r_0) + \sum_{i=1}^3 \frac{\sigma_i(\sigma_j + \sigma_i)(\sigma_k + \sigma_i)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \times \Phi_i(r + r_0 - 2a, \tau), \quad (A7)$$

$$\rho^e(*, \tau|r_0) = k_a \sum_{i=1}^3 \frac{\sigma_i}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \Phi_i(r_0 - a, \tau), \quad (A8)$$

$$\rho^e(*, \tau|*) = - \sum_{i=1}^3 \frac{\sigma_i(\sigma_j + \sigma_k)}{(\sigma_j - \sigma_i)(\sigma_k - \sigma_i)} \Phi_i(0, \tau). \quad (A9)$$

Here, $f_{\text{ref}}(r, \tau|r_0)$ is the solution of the nonreactive diffusion equation for the reflective boundary condition $f_{\text{ref}} = [e^{-(r-r_0)^2/4\tau} + e^{-(r+r_0-2a)^2/4\tau}] / \sqrt{4\pi\tau}$. Note that $f_{\text{ref}}(r, \tau|r_0)$ in 1D can be obtained by $a=0$. The variables of σ_1 , σ_2 , and σ_3 are roots of the corresponding cubic equations $\Delta(\sigma)$, which are given by

$$\Delta_{3D_ESF}(\sigma) = (\sigma + k_a + k_q + 1/a)(\sigma^2 + k_d - F^2 + k_0 - k_0') - k_a k_d, \quad (A10)$$

$$\Delta_{3D_GSF}(\sigma) = (\sigma + k_a + 1/a)(\sigma^2 + k_d - F^2) - k_a k_d, \quad (A11)$$

$$\Delta_{3D_ES}(\sigma) = (\sigma + k_a + k_q + 1/a)(\sigma^2 + k_d + k_0 - k_0') - k_a k_d, \quad (A12)$$

$$\Delta_{1D_ES}(\sigma) = (\sigma + k_a + k_q)(\sigma^2 + k_d + k_0 - k_0') - k_a k_d, \quad (A13)$$

$$\Delta_{1D_GSF}(\sigma) = (\sigma + k_a - F)(\sigma^2 + k_d - F^2) - k_a k_d, \quad (A14)$$

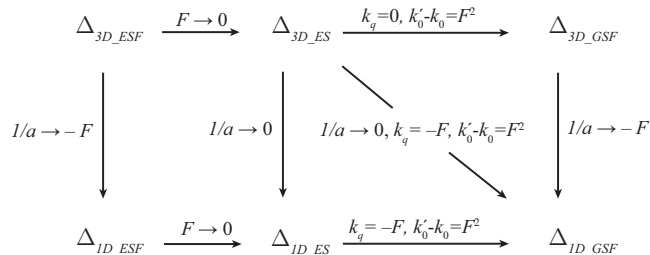


FIG. 3. The relationship diagram of various diffusion-influenced systems: the excited- (1D_ESF, 3D_ESF) and ground-state systems (1D_GSF, 3D_GSF) with an external field in 1D and 3D and the field-free excited-state systems in 1D (1D_ES) and 3D (3D_ES).

$$\Delta_{1D_ESF}(\sigma) = (\sigma + k_a + k_q - F)(\sigma^2 + k_d - F^2 + k_0 - k_0') - k_a k_d. \quad (A15)$$

As expected, Δ_{3D_ES} and Δ_{1D_ES} are obtained by substituting $F=0$ in Δ_{3D_ESF} and Δ_{1D_ESF} , respectively. Interestingly, 1D results can be obtained by substituting $1/a=-F$ in 3D results. One also can see that Δ_{3D_GSF} can be obtained by substituting $k_q=0$ and $k'_0-k_0=F^2$ in Δ_{3D_ES} , while Δ_{1D_GSF} can be obtained by $k_q=-F$ and $k'_0-k_0=F^2$ in Δ_{1D_ES} . These relations are summarized in Fig. 3. Since the kinetic transition occurs when $\Delta(0)=0$, the relations in Fig. 3 can be applied to find the transition condition.

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