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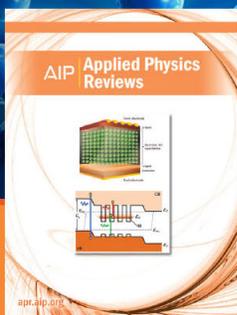
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# An accurate expression for the rates of diffusion-influenced bimolecular reactions with long-range reactivity

Chang Yun Son,<sup>1</sup> Jaehoon Kim,<sup>1</sup> Ji-Hyun Kim,<sup>1</sup> Jun Soo Kim,<sup>2</sup> and Sangyoub Lee<sup>1,a)</sup>

<sup>1</sup>Department of Chemistry, Seoul National University, Seoul 151-747, South Korea

<sup>2</sup>Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, South Korea

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By using the recently developed method for solving the Fredholm integral equations of the second kind, we derive a very accurate expression for the steady-state rate constant of diffusion-influenced bimolecular reactions involving long-range reactivity. We consider the general case in which the reactants interact via an arbitrary central potential and hydrodynamic interaction. The rate expression becomes exact in the two opposite limits of small and large reactivity, and also performs very well in the intermediate regime. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4802584>]

## I. INTRODUCTION

The bimolecular energy or electron transfer occurs at a range of separation between donor and acceptor molecules.<sup>1</sup> When the reaction medium is very viscous or the inherent transfer process is very fast, the overall rate of the transfer reaction depends on the relative diffusion rate of the reactant molecules. Then the steady-state rate constant  $k_s$  can be determined by solving the Smoluchowski equation:<sup>1</sup>

$$D r^{-2} \frac{\partial}{\partial r} r^2 h(r) e^{-U(r)} \frac{\partial}{\partial r} e^{U(r)} \rho(r) = S(r) \rho(r). \quad (1.1)$$

$\rho(r)$  denotes the nonequilibrium pair correlation function; if the bulk number density of the acceptor molecules is  $[A]$ ,  $4\pi r^2 \rho(r) [A] dr$  gives the number of A molecules around a donor molecule D located at a distance between  $r$  and  $r + dr$ .  $U(r)$  denotes an arbitrary central interaction potential in units of  $k_B T$ , with  $k_B$  and  $T$  denoting the Boltzmann constant and the absolute temperature. The relative diffusion coefficient at large separation is  $D$ , but its value decreases with decreasing  $r$  due to the hydrodynamic interaction, which is described by the function  $h(r)$ . The sink function  $S(r)$  denotes the energy or electron transfer rate when the distance between D and A is  $r$ . The steady-state rate constant  $k_s$  is related to  $\rho(r)$  as<sup>2,3</sup>

$$k_s = \int_{\sigma}^{\infty} dr 4\pi r^2 S(r) \rho(r). \quad (1.2)$$

The exact solution of Eq. (1.1) is known only for certain types of  $S(r)$  in the case of noninteracting reactants with  $U(r) = 0$  and  $h(r) = 1$ , and for  $S(r) \propto r^{-6}$  in the case when  $U(r) = r_C/r$  and  $h(r) = 1$ ;<sup>4</sup>  $r_C$  is the Onsager distance given by  $r_C = z_1 z_2 e^2 / (4\pi \epsilon_0 \epsilon_r k_B T)$ , where  $z_1 e$  and  $z_2 e$  are the charges of the reactants,  $\epsilon_0$  is the permittivity of vacuum, and  $\epsilon_r$  is the relative permittivity of the medium. Zharikov and Shokhirev<sup>5</sup> derived very narrow upper and lower bounds to  $k_s$  in the case when  $h(r) = 1$ .

The purpose of this paper is to illustrate the usefulness of the new solution method for the Fredholm integral equa-

tions of the second kind that were proposed recently by us.<sup>6,7</sup> It will be shown that the method provides a very accurate expression for  $k_s$  in the fully general case. In Sec. II, we will briefly summarize the new solution method for the integral equations. The general expression for  $k_s$  is then presented in Sec. III, and its accuracy is compared against the known exact expressions for  $k_s$  and the upper and lower bounds given by Zharikov and Shokhirev in Sec. IV.

## II. THE SOLUTION METHOD FOR FREDHOLM INTEGRAL EQUATIONS

An inhomogeneous Fredholm integral equation of the second kind is given as

$$f(x) = g(x) - \int_a^b dy \epsilon K(x, y) f(y), \quad (2.1)$$

where  $f(x)$  is the function that needs to be determined and  $\epsilon$  is a smallness parameter. When  $\epsilon \rightarrow 0$ ,  $f(x)$  reduces to the unperturbed solution  $g(x)$ . When a closed form analytic solution is not available, one may resort to the usual iterative method to obtain<sup>8</sup>

$$f(x) = g(x) - \epsilon \int_a^b dy_1 K(x, y_1) g(y_1) + \epsilon^2 \int_a^b dy_1 K(x, y_1) \times \int_a^b dy_2 K(y_1, y_2) g(y_2) + \dots \quad (2.2)$$

This perturbative solution may converge slowly or even diverge. One then usually makes Padé approximation to obtain a sensible result.

Recently, we proposed a new method of solution for Eq. (2.1) that gives very accurate results if  $f(x)$  is a monotonically varying nonzero function.<sup>6</sup> The idea is very simple. We first rewrite Eq. (2.1) as

$$f(x) = g(x) - f(x) \int_a^b dy \epsilon K(x, y) [f(y)/f(x)]. \quad (2.3)$$

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: sangyoub@snu.ac.kr

This equation is solved formally to give

$$f(x) = g(x) \left\{ 1 + \int_a^b dy \varepsilon K(x, y) [f(y)/f(x)] \right\}^{-1}. \quad (2.4)$$

To get an explicit result, we then replace the ratio  $f(y)/f(x)$  by  $f_a(y)/f_a(x)$  where  $f_a(x)$  is an approximate form for  $f(x)$ :

$$f(x) \cong g(x) \left\{ 1 + \int_a^b dy \varepsilon K(x, y) [f_a(y)/f_a(x)] \right\}^{-1}. \quad (2.5)$$

An immediate choice for  $f_a(x)$  that will give accurate results in the  $\varepsilon \rightarrow 0$  limit is given by the first few terms in the perturbation series in Eq. (2.2). We have found that this procedure gives more accurate results than the Padé approximation method for the same computational cost. The reason is that (i) Eq. (2.5) has the same formal structure as the exact relation in Eq. (2.4) and (ii) the error caused by using the approximate function  $f_a(x)$  would be partially offset because it enters as a ratio.

However, we have more flexibility in using Eq. (2.5), in that  $f_a(x)$  may be chosen to be an approximate form of  $f(x)$  in the large  $\varepsilon$  limit. This choice would naturally produce a solution that is accurate in the large  $\varepsilon$  limit, but such a solution also gives an exact result in the opposite  $\varepsilon \rightarrow 0$  limit as can be seen from Eq. (2.5).

### III. A GENERAL EXPRESSION FOR THE RATE CONSTANT

We will consider the general case in which the reaction sink function contains the contact reaction term as well as the long-range reaction term:

$$S(r) = \frac{k_\sigma}{g(\sigma)} \frac{\delta(r - \sigma)}{4\pi\sigma^2} + S_L(r). \quad (3.1)$$

As in Ref. 6, we introduce the following transformations:

$$\tilde{r}(r) = \left\{ \int_r^\infty dr_1 [r_1^2 h(r_1) e^{-U(r_1)}]^{-1} \right\}, \quad (3.2)$$

$$\tilde{\rho}(\tilde{r}) = e^{U(r)} \rho(r). \quad (3.3)$$

With these transformations, Eq. (1.1) and the associated boundary conditions,  $\lim_{r \rightarrow \infty} \rho(r) = 1$  and  $\partial[e^{U(r)} \rho(r)]/\partial r|_{r=\sigma} = 0$ , can be written as

$$D\varphi(r) \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \tilde{r}^2 \frac{\partial}{\partial \tilde{r}} \tilde{\rho}(\tilde{r}) = S(\tilde{r}) \tilde{\rho}(\tilde{r}), \quad (3.4)$$

$$\lim_{\tilde{r} \rightarrow \infty} \tilde{\rho}(\tilde{r}) = 1, \quad (3.5)$$

$$\partial \tilde{\rho}(\tilde{r}) / \partial \tilde{r}|_{\tilde{r}=\tilde{\sigma}} = 0, \quad (3.6)$$

where  $\varphi(r) \equiv (\tilde{r}/r)^4 e^{2U(r)}/h(r)$  and  $\tilde{\sigma} = \tilde{r}(\sigma)$ . For notational convenience, we will not distinguish a function of  $\tilde{r}$  from that

of  $r$  representing the same quantity; that is,  $\varphi(\tilde{r}(r)) = \varphi(r)$  and so on. The rate constant in Eq. (1.2) and the sink function in Eq. (3.1) can be expressed as

$$k_s = \int_{\tilde{\sigma}}^\infty d\tilde{r} 4\pi \tilde{r}^2 \varphi(\tilde{r})^{-1} S(\tilde{r}) \tilde{\rho}(\tilde{r}), \quad (3.7)$$

$$S(\tilde{r}) = k_\sigma \varphi(\tilde{\sigma}) \frac{\delta(\tilde{r} - \tilde{\sigma})}{4\pi \tilde{\sigma}^2} + S_L(\tilde{r}). \quad (3.8)$$

It can be shown that the reflecting boundary condition at  $\tilde{\sigma}$  in Eq. (3.6) and the contact sink term in Eq. (3.8) can be combined to the radiative boundary condition:

$$\frac{\partial}{\partial \tilde{r}} \tilde{\rho}(\tilde{r}) \Big|_{\tilde{r}=\tilde{\sigma}} = \frac{k_\sigma}{4\pi \tilde{\sigma}^2 D} \tilde{\rho}(\tilde{\sigma}). \quad (3.9)$$

With this boundary condition, we need to keep only the long-range reaction sink term  $S_L(\tilde{r})$  in Eq. (3.8).

To obtain the expression for  $\tilde{\rho}(\tilde{r})$ , we first multiply Eq. (3.4) by  $\tilde{r}^2/D\varphi(\tilde{r})$  and integrate the resulting equation over  $\tilde{r}$  from  $\tilde{\sigma}$  to  $\tilde{r}_1$ . This gives

$$\frac{\partial}{\partial \tilde{r}_1} \tilde{\rho}(\tilde{r}_1) = \frac{1}{\tilde{r}_1^2} \frac{k_\sigma}{4\pi D} \tilde{\rho}(\tilde{\sigma}) + \frac{1}{\tilde{r}_1^2} \int_{\tilde{\sigma}}^{\tilde{r}_1} d\tilde{r}_0 \frac{\tilde{r}_0^2 S_L(\tilde{r}_0)}{D\varphi(\tilde{r}_0)} \tilde{\rho}(\tilde{r}_0). \quad (3.10)$$

We then integrate Eq. (3.10) over  $\tilde{r}_1$  from  $\tilde{r}$  to  $\infty$ . After some algebra we obtain

$$\begin{aligned} \tilde{\rho}(\tilde{r}) &= \left( 1 - \frac{\nu_\sigma \tilde{\sigma}}{\tilde{r}} \right) - \int_{\tilde{\sigma}}^\infty d\tilde{r}_0 \left( \frac{\tilde{r}_0}{\max(\tilde{r}, \tilde{r}_0)} - \frac{\nu_\sigma \tilde{\sigma}}{\tilde{r}} \right) \\ &\quad \times \frac{\tilde{r}_0 S_L(\tilde{r}_0)}{D\varphi(\tilde{r}_0)} \tilde{\rho}(\tilde{r}_0), \end{aligned} \quad (3.11)$$

where  $\nu_\sigma$  is defined as

$$\nu_\sigma \equiv \frac{k_\sigma}{4\pi D \tilde{\sigma} + k_\sigma}. \quad (3.12)$$

Equation (3.11) is a Fredholm integral equation of the second kind. The solution method described in Sec. II gives

$$\begin{aligned} \tilde{\rho}(\tilde{r}) &\cong \left( 1 - \frac{\nu_\sigma \tilde{\sigma}}{\tilde{r}} \right) \left[ 1 + \int_{\tilde{\sigma}}^\infty d\tilde{r}_0 \left( \frac{\tilde{r}_0}{\max(\tilde{r}, \tilde{r}_0)} - \frac{\nu_\sigma \tilde{\sigma}}{\tilde{r}} \right) \right. \\ &\quad \left. \times \frac{\tilde{r}_0 S_L(\tilde{r}_0)}{D\varphi(\tilde{r}_0)} \frac{\tilde{\rho}_a(\tilde{r}_0)}{\tilde{\rho}_a(\tilde{r})} \right]^{-1}. \end{aligned} \quad (3.13)$$

The simplest choice for  $\tilde{\rho}_a(\tilde{r})$  is

$$\tilde{\rho}_a(\tilde{r}) = 1 - \nu_\sigma \tilde{\sigma} / \tilde{r}. \quad (3.14)$$

As discussed in Sec. II, this choice of  $\tilde{\rho}_a(\tilde{r})$  would give a reasonably good solution for small  $S_L(\tilde{r})$  and large  $D$ . By substituting Eq. (3.14) into Eq. (3.13), we obtain

$$\begin{aligned} \tilde{\rho}_0(\tilde{r}) &= \left( 1 - \frac{\nu_\sigma \tilde{\sigma}}{\tilde{r}} \right) \left\{ 1 + \frac{1}{D} \left[ \int_{\tilde{\sigma}}^{\tilde{r}} d\tilde{r}_0 \frac{(\tilde{r}_0 - \nu_\sigma \tilde{\sigma})^2 S_L(\tilde{r}_0)}{(\tilde{r} - \nu_\sigma \tilde{\sigma}) \varphi(\tilde{r}_0)} \right. \right. \\ &\quad \left. \left. + \int_{\tilde{r}}^\infty d\tilde{r}_0 (\tilde{r}_0 - \nu_\sigma \tilde{\sigma}) \frac{S_L(\tilde{r}_0)}{\varphi(\tilde{r}_0)} \right] \right\}^{-1}. \end{aligned} \quad (3.15)$$

With this approximate expression of  $\tilde{\rho}(\tilde{r})$ , Eq. (3.7) gives

$$k_s \cong k_\sigma \tilde{\rho}_0(\tilde{\sigma}) + \int_{\tilde{\sigma}}^{\infty} d\tilde{r} 4\pi \tilde{r}^2 \varphi(\tilde{r})^{-1} S_L(\tilde{r}) \tilde{\rho}_0(\tilde{r}). \quad (3.16)$$

To get a solution that is applicable to the case of large reactivity [large  $S_L(\tilde{r})$  and small  $D$ ], we first note that the asymptotic form of  $\tilde{\rho}(\tilde{r})$  at large distance is given by  $\tilde{\rho}(\tilde{r}) = 1 - k_s/4\pi D\tilde{r}$ , because the steady-state inward flux is equal to  $k_s$ . We thus assume an expression for  $\tilde{\rho}(\tilde{r})$  given as

$$\tilde{\rho}(\tilde{r}) = \left(1 - \frac{\nu\tilde{\sigma}}{\tilde{r}}\right) \exp\left[-\int_{\tilde{r}}^{\infty} d\tilde{r} \chi(\tilde{r})\right], \quad (3.17)$$

where  $\nu = k_s/4\pi D\tilde{\sigma}$  and  $\chi(\tilde{r})$  is a function that decays rapidly enough that  $\lim_{\tilde{r} \rightarrow \infty} \int_{\tilde{r}}^{\infty} d\tilde{r} \chi(\tilde{r}) = 0$ . By substituting Eq. (3.17) into Eq. (3.4), we can obtain the equation for  $\chi(\tilde{r})$  as

$$\frac{\partial \chi(\tilde{r})}{\partial \tilde{r}} + \frac{2}{\tilde{r} - \nu\tilde{\sigma}} \chi(\tilde{r}) + \chi(\tilde{r})^2 = \frac{S_L(\tilde{r})}{D\varphi(\tilde{r})}. \quad (3.18)$$

The outer boundary condition in Eq. (3.5) is automatically satisfied. From the inner boundary condition in Eq. (3.9), we have

$$\chi(\tilde{\sigma}) = \frac{k_\sigma}{4\pi\tilde{\sigma}^2 D} - \frac{\nu}{\tilde{\sigma}(1-\nu)}. \quad (3.19)$$

When  $S_L(r) = 0$ ,  $\nu \rightarrow \nu_\sigma$  and  $\chi(\tilde{r}) \rightarrow 0$ . On the other hand, when  $S_L(r)$  becomes large, we expect that  $\chi(\tilde{r})$  also becomes large. In the strong sink limit, the terms linear in  $\chi(\tilde{r})$  in Eq. (3.18) may be neglected compared to the  $\chi(\tilde{r})^2$  term. In this limit, we thus have

$$\chi(r) \cong \left[\frac{S_L(\tilde{r})}{D\varphi(\tilde{r})}\right]^{1/2}. \quad (3.20)$$

We now take as the zeroth-order solution,

$$\tilde{\rho}^{(0)}(\tilde{r}) = \left(1 - \frac{\nu^{(0)}\tilde{\sigma}}{\tilde{r}}\right) \exp\left[-\int_{\tilde{r}}^{\infty} d\tilde{r}_1 \left(\frac{S_L(\tilde{r}_1)}{D\varphi(\tilde{r}_1)}\right)^{1/2}\right], \quad (3.21)$$

where  $\nu^{(0)}$  is an approximation to the unknown constant  $\nu$  that is given by

$$\nu^{(0)} = \frac{k_{eq}}{k_{eq} + 4\pi\tilde{\sigma}D}, \quad k_{eq} = \int_{\sigma}^{\infty} dr 4\pi r^2 S(r)g(r). \quad (3.22)$$

By taking  $\tilde{\rho}^{(0)}(\tilde{r})$  as  $\tilde{\rho}_a(\tilde{r})$  in Eq. (3.13), we obtain an improved expression for  $\tilde{\rho}(\tilde{r})$ :

$$\tilde{\rho}^{(1)}(\tilde{r}) = \left(1 - \frac{\nu_\sigma\tilde{\sigma}}{\tilde{r}}\right) \left[1 + \int_{\tilde{\sigma}}^{\infty} d\tilde{r}_0 \left(\frac{\tilde{r}_0}{\max(\tilde{r}, \tilde{r}_0)} - \frac{\nu_\sigma\tilde{\sigma}}{\tilde{r}}\right) \times \frac{\tilde{r}_0 S_L(\tilde{r}_0) \tilde{\rho}^{(0)}(\tilde{r}_0)}{D\varphi(\tilde{r}_0) \tilde{\rho}^{(0)}(\tilde{r})}\right]^{-1}. \quad (3.23)$$

By using this expression for  $\tilde{\rho}(\tilde{r})$  in Eq. (3.7), we can calculate the steady-state rate constant as

$$k_s^{(1)} = k_\sigma \tilde{\rho}^{(1)}(\tilde{\sigma}) + \int_{\tilde{\sigma}}^{\infty} d\tilde{r} 4\pi \tilde{r}^2 \varphi(\tilde{r})^{-1} S_L(\tilde{r}) \tilde{\rho}^{(1)}(\tilde{r}). \quad (3.24)$$

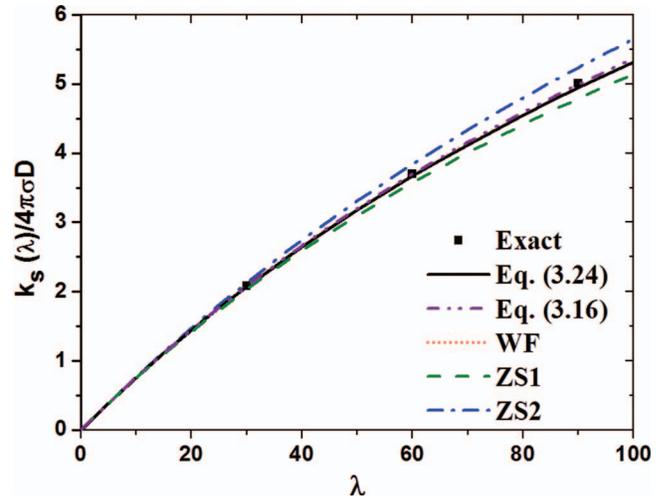


FIG. 1. The steady-state rate constant  $k_s$  of an electron transfer reaction involving a distance-dependent sink function given by  $S(r) = \kappa e^{-2\beta r}$ ; the dimensionless reaction strength parameter  $\lambda$  is defined by  $\lambda = \kappa\pi e^{-2\beta\sigma} (2\beta^2\sigma^2 + 2\beta\sigma + 1)/(D\sigma\beta^3)$ .

We may use this expression for  $k_s^{(1)}$  to obtain an improved value of  $\nu$  as  $\nu^{(1)} = k_s^{(1)}/4\pi D\tilde{\sigma}$ , and then continue the iteration to get the refined solution. However, we have found that in most cases a very accurate solution can be obtained just with  $\nu^{(0)}$  and  $\tilde{\rho}^{(1)}(\tilde{r})$ .

#### IV. NUMERICAL RESULTS

We now evaluate the accuracy of the approximate rate constant expressions in Eqs. (3.16) and (3.24). The numerical integrations can be carried out by noting that

$$\int_{\tilde{\sigma}}^{\infty} d\tilde{r} (\dots) = \int_{\sigma}^{\infty} dr \frac{\varphi(r)^{1/2}}{h(r)^{1/2}} (\dots), \quad (4.1)$$

$$\int_{\tilde{\sigma}}^{\infty} d\tilde{r} 4\pi \tilde{r}^2 (\dots) = \int_{\sigma}^{\infty} dr 4\pi r^2 \varphi(r) e^{-U(r)} (\dots).$$

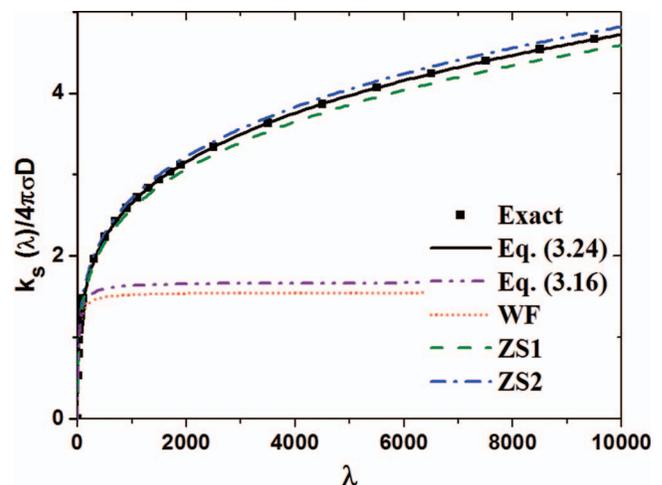


FIG. 2. The steady-state rate constant  $k_s$  of the Förster energy transfer involving a distance-dependent sink function,  $S(r) = \alpha r^{-6}$ ; the dimensionless reaction strength parameter  $\lambda$  is defined by  $\lambda = 4\pi\alpha/(3D\sigma^4)$ .

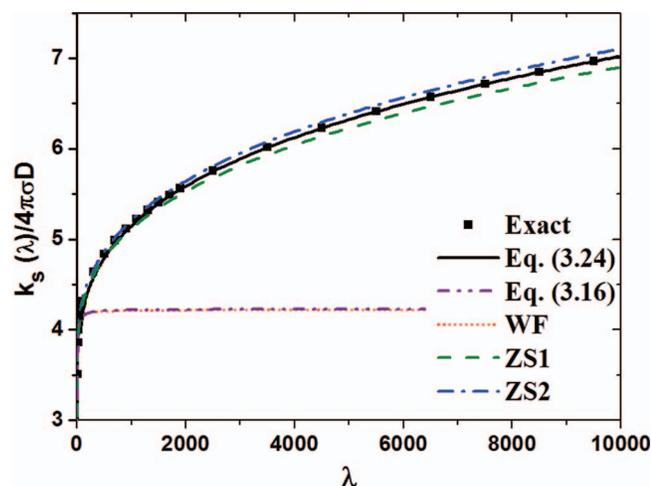


FIG. 3. The steady-state rate constant  $k_s$  of the Förster energy transfer under Coulomb potential  $U(r) = r_C/r$ ; the sink function is given by  $S(r) = \alpha r^{-6}$  and  $\lambda = 4\pi\alpha/(3D\sigma^4)$ .

We will compare the results of Eqs. (3.16) and (3.24) with those obtained from the Wilemski-Fixman (WF) rate expression<sup>9</sup> and the upper and lower bound expressions given by Zharikov and Shokhirev (ZS),<sup>5</sup> as well as with the exact results.

The distance-dependent reactivity of diffusion-influenced electron transfer reactions is often described by an exponential sink function as  $S(r) = \kappa e^{-2\beta r}$ . In the interaction free case with  $U(r) = 0$  and  $h(r) = 1$  for  $r \geq \sigma$ , the exact expression for  $k_s$  is given by<sup>10-12</sup>

$$\frac{k_s}{4\pi D\sigma} = (\beta\sigma)^{-1} \left[ \frac{K_0(x) - \beta\sigma x K_1(x)}{I_0(x) + \beta\sigma x I_1(x)} + \gamma - \ln 2\mu \right], \quad (4.2)$$

where  $I_\nu(x)$  and  $K_\nu(x)$  are the  $\nu$ th-order modified Bessel functions of the first and the second kind,<sup>13</sup> respectively.  $x = \mu^{-1} e^{-\beta\sigma}$ ,  $\mu = (D\beta^2/\kappa)^{1/2}$ , and  $\gamma (=0.5772\dots)$  is the Euler's constant. Figure 1 displays the results of the present, WF, and ZS theories compared to the exact result. In all calculations, we use the dimensionless variables: length in  $\sigma$ , time in  $t_L (= \sigma^2/D)$ , and energy in  $k_B T$ . In Fig. 1, the abscissa  $\lambda$  is a dimensionless reactivity parameter defined by  $\lambda = k_{eq} t_L / \sigma^3$  where  $k_{eq} = \kappa\pi\beta^{-3} e^{-2\beta\sigma} (2\beta^2\sigma^2 + 2\beta\sigma + 1)$ ;  $k_{eq}$  is the equilibrium rate constant defined by Eq. (3.22). The ordinate is  $k_s/4\pi\sigma D$ . For the electron transfer case, the value of  $\lambda$  may range up to 100.<sup>1</sup> We set the value of  $\beta$  to 0.1. It can be seen that both Eqs. (3.16) and (3.24) of the present theory, as well

as the WF theory, give very accurate results for the whole range of  $\lambda$ ; indeed, the resulting three curves are hardly distinguishable. The ZS theory also provides quite narrow lower and upper bounds to  $k_s$ .

When the energy transfer occurs via the dipole-dipole interaction, the orientation-averaged reactivity is usually modeled by the following sink function:

$$S(r) = \kappa_F (r_F/r)^6 \equiv \alpha r^{-6}. \quad (4.3)$$

Here,  $\kappa_F$  is the natural decay rate of an excited donor molecule in the absence of acceptor molecules and  $r_F$  is the Förster radius at which  $\kappa_F$  and the rate of energy transfer are of equal magnitude. For the purpose of present calculations, we need not specify separate values of  $\kappa_F$  and  $r_F$ , and will denote  $\kappa_F r_F^6$  as  $\alpha$ . In the interaction free case with  $U(r) = 0$  and  $h(r) = 1$  for  $r \geq \sigma$ , the exact expression for  $k_s$  is given by<sup>12, 14, 15</sup>

$$\frac{k_s}{4\pi D\sigma} = \frac{2(3\pi^3\lambda)^{1/4}}{[\Gamma(1/4)]^2} \frac{I_{3/4}(u_0)}{I_{-3/4}(u_0)}. \quad (4.4)$$

Here,  $\Gamma(x)$  is the gamma function,<sup>13</sup>  $\lambda$  is a dimensionless reactivity parameter defined by  $\lambda = k_{eq} t_L / \sigma^3$  with  $k_{eq} = 4\pi\alpha/(3\sigma^3)$  and  $u_0 = \sqrt{3\lambda/(16\pi)}$ . Figure 2 displays the results of the present, WF, and ZS theories compared to the exact result. In this case the abscissa  $\lambda (= k_{eq} t_L / \sigma^3)$  is given by  $4\pi\alpha/(3D\sigma^4)$ . For the Förster energy transfer, the value of  $\lambda$  may range over  $10^4$ . Again, our general rate expression given by Eq. (3.24) provides excellent results for the whole range of  $\lambda$ , and the ZS theory provides very narrow lower and upper bounds. Both Eq. (3.16) and the WF theory give reliable results only for very small  $\lambda$ , but still the former is a little better than the latter.

There are two more cases of interest for which an exact expression for the steady-state rate constant is known. One is the case with the Förster energy transfer under Coulomb potential  $U(r) = r_C/r$  but without the hydrodynamic interaction [ $h(r) = 1$ ], and the other case is the Förster energy transfer with contact quenching but without any interaction [ $U(r) = 0$  and  $h(r) = 1$  for  $r \geq \sigma$ ].

Figure 3 displays the results for the Förster energy transfer under an attractive Coulomb potential; the reaction sink function is given by Eq. (4.3) and  $h(r) = 1$ . We set the value of  $r_C$  to  $-4\sigma$ . For this case,  $k_{eq} = (3\lambda\sigma^3/t_L)[2y^3 - e^{-r_C/\sigma}(y + 2y^2 + 2y^3)]$  with  $\lambda = 4\pi\alpha/(3D\sigma^4)$  and  $y = \sigma/r_C$ , and an exact expression for  $k_s$  was given by Doktorov, Kipriyanov, and Burshtein:<sup>4</sup>

$$\frac{k_s}{4\pi D\sigma} = -2b + \frac{(2b-z)M\left(\frac{1}{4} + \frac{b^2}{z}, \frac{1}{2}, z\right) + (4b^2+z)M\left(\frac{5}{4} + \frac{b^2}{z}, \frac{3}{2}, z\right)}{(1+2b+z)M\left(\frac{3}{4} + \frac{b^2}{z}, \frac{3}{2}, z\right) + \left(\frac{4b^2}{3} - z\right)M\left(\frac{3}{4} + \frac{b^2}{z}, \frac{5}{2}, z\right)}. \quad (4.5)$$

Here,  $z = \sqrt{3\lambda/(4\pi)}$ ,  $b = r_C/(4\sigma)$ , and  $M(a, b, z)$  is the Kummer's confluent hypergeometric function.<sup>13</sup>

Figure 4 displays the results for the Förster energy transfer with contact quenching;  $U(r) = 0$  and  $h(r) = 1$  for  $r \geq \sigma$ ,

and the sink function is now given by

$$S(r) = k_\sigma \frac{\delta(r-\sigma)}{4\pi\sigma^2} + \frac{\alpha}{r^6}. \quad (4.6)$$

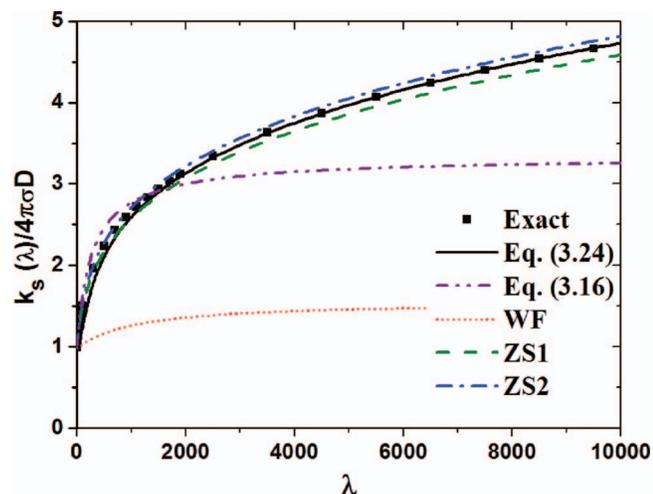


FIG. 4. The steady-state rate constant  $k_s$  of the Förster energy transfer with contact quenching; the sink function is given by  $S(r) = k_\sigma \delta(r - \sigma)/(4\pi\sigma^2) + \alpha r^{-6}$  and  $\lambda = 4\pi\alpha/(3D\sigma^4)$ .

We set the value of  $k_\sigma$  to  $1000\sigma^3/t_L$ . For this case, the exact expression for  $k_s$  was given by Heisel and Miehe:<sup>12</sup>

$$\frac{k_s}{4\pi D\sigma} = \left(\frac{3\lambda}{\pi}\right)^{1/4} \frac{2\pi}{[\Gamma(1/4)]^2} \frac{8\pi D\sigma u_0 I_{3/4}(u_0) + k_\sigma I_{-1/4}(u_0)}{8\pi D\sigma u_0 I_{-3/4}(u_0) + k_\sigma I_{1/4}(u_0)}, \quad (4.7)$$

where  $\lambda = 4\pi\alpha/(3D\sigma^4)$  and  $u_0 = [3\lambda/(16\pi)]^{1/2}$ .

Again, our general rate expression given by Eq. (3.24) and the ZS theory provide excellent results for the whole range of  $\lambda$ , while Eq. (3.16) and the WF theory fail except for very small  $\lambda$ .

## V. CONCLUSION

Very recently we proposed a new method of solution for the Fredholm integral equations of the second kind.<sup>6</sup> In Ref. 6, we showed that the new method provides an accurate expression of the propagator for diffusive dynamics of a pair of particles interacting via an arbitrary central potential and hydrodynamic interaction. By using the propagator ex-

pression, we were able to obtain accurate analytic expressions for the time-dependent rates of diffusion-influenced geminate and bimolecular reactions.<sup>7</sup> In the present work, we confirmed again the utility of the new solution method of the integral equations. We have obtained a general expression for the steady-state rate constant of diffusion-influenced bimolecular reactions involving long-range reactivity; the reactants may interact via an arbitrary central potential and hydrodynamic interaction. The rate expression becomes exact in the two opposite limits of small and large reactivity, and also performs very well in the intermediate regime; its accuracy has been compared against the known exact expressions for the rate constants. We believe that the new procedure for solving the integral equations can be applied to diverse problems; it may provide a convergent solution even in the case where the direct iterative solution method leads to a divergent perturbation series.

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