Effects of a quantum-mechanically driven two-state gating mode on the diffusion-influenced bimolecular reactions

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The reduced distribution function formalism of diffusion-influenced bimolecular reactions is generalized to incorporate a quantum-mechanical gating mode in the description. An analytical expression for the reaction rate coefficient is obtained in the Laplace transform domain for a general initial condition. For a simple reaction model, the time-dependent reaction rate coefficient and the product yield are calculated numerically for two representative initial conditions. Dependence of the rate coefficient and the product branching ratio on various reaction parameters is discussed. © *1997 American Institute of Physics.* [S0021-9606(97)50247-9]

I. INTRODUCTION

When the inherent reaction step proceeds very rapidly upon the contact of reactant molecules, the diffusive encounter rate can influence the overall reaction rate. A theory for the kinetics of diffusion-influenced reactions was first formulated by Smoluchowski.[1] Since then the theory has been refined and generalized in many aspects:[2–5] e.g., refined modelings of the reaction event by the radiation boundary condition[6] or by the reaction sink function,[7] rigorous formulations of the rate theory based on hierarchical kinetic equations governing the evolution of reactant molecule distribution functions,[7–11] inclusion of the effects due to long-range intermolecular forces[12] and solvent-mediated hydrodynamic interactions,[13,14] consideration of orientation-dependent reactivity of reactant molecules,[15–19] and so on.

Another extension of the theory that has attracted much attention is to include the effect of structural fluctuation in reactant molecules that may dynamically modulate their intrinsic reactivity.[19–26] In enzyme–substrate reactions, for example, the enzyme molecule may have side chains that can change the binding site accessibility. Motions of such side chains constitute a *gating mode* which *opens* and *closes* the binding site of substrate molecules.

A simple model for such gated diffusion-influenced reactions was first proposed by McCammon and Northrup.[20,21] They considered a bimolecular reaction between molecules of species A and B:

$$A + B \rightarrow P, \tag{1.1}$$

where B molecules have a fluctuating reactivity due to the gating dynamics of an internal mode. For simplicity, it was assumed that the fluctuations in the reactivity of B molecules can be described as a two-state process and that the switching on and off of the reactivity can be described by a time-dependent function $h(t)$, which alternates between two values, 0 and 1. Later, Szabo *et al.*[22] modified the model by assuming that the dynamics of the gate between the two states can be described by the first-order rate equation

$$B_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} B_2. \tag{1.2}$$

Only one of the two species, say B_1, can react with A, and k_{12} and k_{21} are the rate constants for the closing and opening of the gate. For this stochastically gated diffusion-influenced reaction, Szabo *et al.*[22] obtained an analytical expression for the steady-state reaction rate coefficient. Kim and Lee[23] considered the same model using the reduced distribution function (RDF) formalism and obtained the time-dependent reaction rate coefficient in the Laplace transform domain, which reduces to Szabo *et al.*'s result in the steady-state limit. Recently, Zhou and Szabo[24] reinvestigated the kinetics of the stochastically gated reaction in the pseudo-first-order case, and found that the kinetics varies depending on whether the deficient species (e.g., a protein) or the excess species (e.g., a ligand) is gated. It appears that the reaction goes slower in the case of gated protein than in the case of gated ligand. Berezhkovskii *et al.*[26] ascribed the slowdown of the reaction process in the gated protein case to the correlation between the gating coordinates.

Lee and Karplus[19] extended the formulation of gated diffusion-influenced reaction to the case involving a continuous gating coordinate. It was assumed that the motion along the gating coordinate is diffusive and that the reaction channel is open only at some highly localized section of the coordinate. Such a reaction model may be appropriate for enzyme–substrate reactions involving a pacman-like enzyme; for example, in enzymes such as lysozyme, a loose damped vibrational mode may open and close the active site cleft.[27]
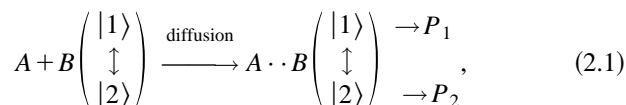
In this article, we propose another variant of the gated reaction model. We consider a case where the transition between the two states B_1 and B_2 in Eq. (1.2) is a nondissipative quantum process. For example, the reactivity of a B molecule can be modulated if it undergoes a rapid intramolecular charge transfer process. In such a case the transition between B_1 and B_2 states needs to be described by the quantum-Liouville equation with an appropriate Hamiltonian for the quantum gating mode.

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This article is organized as follows. In Sec. II, a set of reaction kinetic equations is derived by using the RDF formalism[11] that is generalized to incorporate the quantum-mechanically gated dynamics. In Sec. III, an analytical expression for the time-dependent reaction rate coefficient is obtained in the Laplace transform domain for a general initial condition. In Sec. IV, the rate expressions are simplified for a simple reaction model. In some limiting cases, explicit analytical expressions for the rate coefficient are obtained in the time domain. In Sec. V two representative initial conditions are considered. In the first case, B molecules are assumed to be distributed in equilibrium with equal populations in the B_1 and B_2 states, and the A molecules are sensitized suddenly at time zero. In the second case, B molecules are produced at time zero exclusively in the B_1 state (e.g., by photoexcitation), and then evolve reversibly between the B_1 and B_2 states and react with A molecules. For these initial conditions formal expressions for the product yields are obtained in the pseudo-first-order case. In Sec. VI, we evaluate the rate coefficient and the product yield numerically and investigate their dependence on various reaction parameters.

II. DERIVATION OF KINETIC EQUATIONS

We consider the reaction scheme

$$
A+B\begin{pmatrix}|1\rangle\\ \updownarrow\\ |2\rangle\end{pmatrix}\xrightarrow{\text{diffusion}} A\cdot\cdot B\begin{pmatrix}|1\rangle\\ \updownarrow\\ |2\rangle\end{pmatrix}\begin{array}{c}\rightarrow P_1\\ \\ \rightarrow P_2\end{array}, \tag{2.1}
$$

where P_1 and P_2 are the products of the reaction of A molecules with B molecules in the quantum states $|1\rangle$ and $|2\rangle$, respectively. The two states of a B molecule, $|1\rangle$ and $|2\rangle$, are the diabatic states, and the quantum-mechanical evolution

between the two states is governed by a quantum-Liouville equation. The Hamiltonian governing the quantum-mechanical evolution of the internal states of a B molecule is assumed to be given by a simple two-state model Hamiltonian, which has a 2×2 matrix representation in the basis $\{|1\rangle,|2\rangle\}$,

$$
\mathbf{H}=\begin{pmatrix}\epsilon_1 & \Delta\\ \Delta* & \epsilon_2\end{pmatrix}, \tag{2.2}
$$

where ϵ_1 and ϵ_2 are the energies of the diabatic states, and Δ is the coupling matrix element between the two diabatic states. The superscript * denotes a complex conjugate. An appropriate form of Δ can be chosen for the specific problem under consideration. For instance, if the two-state model refers to intramolecular proton transfer, the coupling matrix element may depend on the internuclear distance between donor and acceptor moieties in the B molecule. However, if we consider a transition between two electronic states, the coupling constant will be given by the product of the transition dipole moment and the external electric field within the electric dipole approximation.

Suppose that there are N_A^0 A molecules and N_B^0 B molecules in solution at time zero. We label the A and B molecules by the indices i and j, where $1\leqslant i\leqslant N_A^0$ and $1\leqslant j\leqslant N_B^0$. In order to represent the quantum states of a B molecule or a pair of $A-B$ molecules we use the basis $\{|1\rangle,|2\rangle\}$. Since it is impossible to have exact information on the initial conditions of all reactant molecules, we have to rely on a probabilistic description for the status of a reactant molecule at a later time t. We first introduce the one-particle probability density function, $P_{A_i}(\mathbf{r}_A,t)$; $P_{A_i}(\mathbf{r}_A,t)d\mathbf{r}_A$ gives the probability that the molecule A_i has not reacted until time t and is located within a volume element $d\mathbf{r}_A$ at $\mathbf{r}_A$. The time evolution equation of P_{A_i} is given by[11,28,29]

$$
\frac{\partial}{\partial t}P_{A_i}(\mathbf{r}_A,t)=L_A P_{A_i}(\mathbf{r}_A,t)-\sum_{j=1}^{N_B^0}\int d\mathbf{r}_B\ \mathrm{Tr}\ \tfrac{1}{2}[\mathbf{S}_{AB}(\mathbf{r}_A,\mathbf{r}_B),\mathbf{P}_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)]_+ . \tag{2.3}
$$

Here the first term on the right hand side (RHS) of Eq. (2.3) represents the change of P_{A_i} due to thermal motion of A_i. In this work we assume that all the nonreactive thermal evolution operators are given by the Smoluchowski operators. For example, L_A is given by $L_A=D_A\nabla^2$, with D_A denoting the diffusion constant of the A molecule, when the potential of mean force is negligible. The second term of the RHS denotes the change due to reaction of A_i with any of B molecules located at $\mathbf{r}_B$ at time t. Since we need to take account of the internal quantum states of the B molecule as well as the classical configurational variables in treating the pair correlation between A and B molecules, we introduce the two-

particle probability distribution matrix $\mathbf{P}_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)$ instead of the two-particle probability density function,

$$
\mathbf{P}_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)=\begin{pmatrix}P_{A_iB_j}^{11}(\mathbf{r}_A,\mathbf{r}_B,t) & P_{A_iB_j}^{12}(\mathbf{r}_A,\mathbf{r}_B,t)\\ P_{A_iB_j}^{21}(\mathbf{r}_A,\mathbf{r}_B,t) & P_{A_iB_j}^{22}(\mathbf{r}_A,\mathbf{r}_B,t)\end{pmatrix}. \tag{2.4}
$$

The diagonal element $P_{A_iB_j}^{nn}(\mathbf{r}_A,\mathbf{r}_B,t)$ $(n=1,2)$ represents the probability density that A_i and B_j molecules are found at $\mathbf{r}_A$ and $\mathbf{r}_B$ at time t, with the quantum state of B_j given by $|n\rangle$. The off-diagonal matrix elements represent the coherence between the two states $|1\rangle$ and $|2\rangle$ in the statistical mix-

ture describing the probabilistic state of the $A_i - B_j$ pair. The reaction sink matrix $\mathbf{S}_{AB}(\mathbf{r}_A, \mathbf{r}_B)$ is given by[28,29]

$$\mathbf{S}_{AB}(\mathbf{r}_A, \mathbf{r}_B) = S_1(\mathbf{r}_A, \mathbf{r}_B)|1\rangle\langle 1| + S_2(\mathbf{r}_A, \mathbf{r}_B)|2\rangle\langle 2|, \quad (2.5)$$

where $S_n(\mathbf{r}_A, \mathbf{r}_B)$ represents the rate of reaction between an A molecule at $\mathbf{r}_A$ and a B molecule at $\mathbf{r}_B$ whose internal state is given by $|n\rangle$. In Eq. (2.3) Tr denotes the trace operation, and $[\ ]_+$ denotes the anticommutator defined by $[\mathbf{A}, \mathbf{B}]_+ \equiv \mathbf{AB} + \mathbf{BA}$.

Since B molecules undergo quantum-mechanical evolution between two states in addition to the thermal evolution and chemical reaction, evolution equation for the one-particle probability distribution matrix $\mathbf{P}_{B_j}(\mathbf{r}_B, t)$ for the molecule B_j is written as

$$\frac{\partial}{\partial t}\mathbf{P}_{B_j}(\mathbf{r}_B, t)$$

$$= L_B \mathbf{P}_{B_j}(\mathbf{r}_B, t) - \frac{i}{\hbar}[\mathbf{H}, \mathbf{P}_{B_j}(\mathbf{r}_B, t)]$$

$$- \sum_{i=1}^{N_A^0} \int d\mathbf{r}_A \tfrac{1}{2}[\mathbf{S}_{AB}(\mathbf{r}_A, \mathbf{r}_B), \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t)]_+. \quad (2.6)$$

The first term on the RHS describes the change due to the thermal motion of B_j. The second term represents the change due to the quantum-mechanical transition of B_j between two internal states under the governing Hamiltonian in Eq. (2.2). $[\ ]$ denotes the commutator defined by $[\mathbf{A}, \mathbf{B}] \equiv \mathbf{AB} - \mathbf{BA}$. The third term describes the change due to the reaction of B_j with any of A molecules located at $\mathbf{r}_A$.

The two-particle probability distribution matrix $\mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t)$ evolves according to

$$\frac{\partial}{\partial t}\mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t) = L_{AB}\mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t) - \frac{i}{\hbar}[\mathbf{H}, \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t)] - \frac{1}{2}[\mathbf{S}_{AB}(\mathbf{r}_A, \mathbf{r}_B), \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t)]_+$$

$$- \sum_{\substack{k=1 \\ k \neq j}}^{N_B^0} \int d\mathbf{r}_B' \, \mathrm{Tr}\, \frac{1}{2}[\mathbf{S}_{AB}(\mathbf{r}_A, \mathbf{r}_B'), \mathbf{P}_{B_k(A_i)}(\mathbf{r}_B', t|\mathbf{r}_A)]_+ \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t)$$

$$- \sum_{\substack{l=1 \\ l \neq i}}^{N_A^0} \int d\mathbf{r}_A' \, \mathrm{Tr}\, \tfrac{1}{2}[\mathbf{S}_{AB}(\mathbf{r}_A', \mathbf{r}_B), \mathbf{P}_{A_l(B_j)}(\mathbf{r}_A', t|\mathbf{r}_B)]_+ \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t). \quad (2.7)$$

The first term on the RHS represents the change due to thermal diffusive motion of the $A_i - B_j$ pair; L_{AB} is the governing Smoluchowski operator. The second term represents the change of $\mathbf{P}_{A_j B_j}(\mathbf{r}_A, \mathbf{r}_B, t)$ caused by the quantum-mechanical evolution in the internal state of B_j. The third term represents the change due to reaction between A_i and B_j via the two channels described in Eq. (2.1). The fourth term takes account of the competitive reaction events between A_i and any of the B molecules other than B_j. $\mathbf{P}_{B_k(A_i)}(\mathbf{r}_B', t|\mathbf{r}_A)$ denotes the conditional probability distribution matrix for the molecule B_k given that A_i is at $\mathbf{r}_A$ at time t. The fifth term has similar meaning. In these last two terms, we have introduced dynamic superposition approximations[8–11,30] to truncate the hierarchical structure of the evolution equations for many-particle probability density functions. Thereby we have obtained a closed set of evolution equations as given by Eqs. (2.3), (2.6), and (2.7).

In the absence of any external field that makes the reaction system nonuniform, the following relations hold between the number densities, denoted as $[A]$ and $[B]$, and the one-particle probability density functions:

$$\sum_{i=1}^{N_A^0} P_{A_i}(\mathbf{r}_A, t) = [A], \quad (2.8)$$

$$\sum_{j=1}^{N_B^0} \mathrm{Tr}\, \mathbf{P}_{B_j}(\mathbf{r}_B, t) = [B]. \quad (2.9)$$

Then we can also define the pair correlation matrix $\boldsymbol{\rho}_{AB}(r, t)$ between A and B molecules by

$$\sum_{i=1}^{N_A^0} \sum_{j=1}^{N_B^0} \mathbf{P}_{A_i B_j}(\mathbf{r}_A, \mathbf{r}_B, t) = [A][B]\boldsymbol{\rho}_{AB}(|\mathbf{r}_B - \mathbf{r}_A|, t);$$

$$\sum_{\substack{k=1 \\ k \neq j}}^{N_B^0} \mathbf{P}_{B_k(A_i)}(\mathbf{r}_B', t|\mathbf{r}_A) = [B]\boldsymbol{\rho}_{AB}(|\mathbf{r}_B' - \mathbf{r}_A|, t); \quad (2.10)$$

$$\sum_{\substack{l=1 \\ l \neq i}}^{N_A^0} \mathbf{P}_{A_l(B_j)}(\mathbf{r}_A', t|\mathbf{r}_B) = [A]\boldsymbol{\rho}_{AB}(|\mathbf{r}_A' - \mathbf{r}_B|, t).$$

We can obtain the rate equations for $[A]$ and $[B]$ from Eqs. (2.3) and (2.6) by summing them over the indices i and j, respectively, and carrying out the trace operation on the equation resulting from Eq. (2.6):

$$\frac{d}{dt}[A] = \frac{d}{dt}[B] = -k_f(t)[A][B]. \quad (2.11)$$

The bimolecular reaction rate coefficient $k_f(t)$ is defined by

$$k_f(t) = \int d\mathbf{r} \ \mathrm{Tr} \ \tfrac{1}{2}[\mathbf{S}_{AB}(r), \boldsymbol{\rho}_{AB}(r,t)]_+ = k_1(t) + k_2(t), \tag{2.12}$$

$$k_n(t) = \int d\mathbf{r} \ S_n(r)\rho_n(r,t) \quad (n=1 \text{ or } 2), \tag{2.13}$$

where $r = |\mathbf{r}_B - \mathbf{r}_A|$, and $\rho_n(r,t)$ is defined by $\rho_n(r,t) = \langle n|\boldsymbol{\rho}_{AB}(r,t)|n\rangle$. It measures the relative population of B molecules in the quantum state $|n\rangle$ at a distance r from the origin where an A molecule is located. We have assumed that the reaction sink depends only on the relative separation of A and B molecules.

Evolution equation for the pair correlation matrix $\boldsymbol{\rho}_{AB}(r,t)$ can be obtained by summing Eq. (2.7) over indices i and j,

$$\frac{\partial}{\partial t}\{[A][B]\boldsymbol{\rho}(r,t)\} = [A][B]L_0(r)\boldsymbol{\rho}(r,t)$$

$$-[A][B]\frac{i}{\hbar}[\mathbf{H}, \boldsymbol{\rho}(r,t)]$$

$$-[A][B]\tfrac{1}{2}[\mathbf{S}(r), \boldsymbol{\rho}(r,t)]_+$$

$$-k_f(t)([A]+[B])[A][B]\boldsymbol{\rho}(r,t). \tag{2.14}$$

We have used Eqs. (2.10) and (2.12) defining the pair correlation matrix and the rate coefficient. We have dropped the subscript AB from $\boldsymbol{\rho}_{AB}$ and $\mathbf{S}_{AB}$ to simplify notations, and have replaced the two-particle Smoluchowski operator L_{AB} with a contracted form in r space:

$$L_0(r) = \left(\frac{\partial}{\partial r} + \frac{2}{r}\right)d(r)\left(\frac{\partial}{\partial r} + \beta\frac{\partial U(r)}{\partial r}\right). \tag{2.15}$$

Here $d(r)$ denotes the relative diffusion coefficient, which depends on r if the hydrodynamic interaction between A and B molecules is included, and $U(r)$ is the potential of mean force. $\beta = 1/k_B T$ with the Boltzmann constant k_B and the absolute temperature T. By using Eq. (2.11) we can simplify Eq. (2.14) to get

$$\frac{\partial}{\partial t}\boldsymbol{\rho}(r,t) = L_0(r)\boldsymbol{\rho}(r,t) - \frac{i}{\hbar}[\mathbf{H}, \boldsymbol{\rho}(r,t)]$$

$$-\frac{1}{2}[\mathbf{S}(r), \boldsymbol{\rho}(r,t)]_+. \tag{2.16}$$

III. REACTION RATE COEFFICIENT IN THE LAPLACE DOMAIN

For an easier algebraic manipulation, it is convenient to write the pair correlation matrix $\boldsymbol{\rho}(r,t)$ in the form of a column vector as

$$|\rho(r,t)\rangle\rangle = [\rho_{11}(r,t), \rho_{22}(r,t), \rho_{12}(r,t), \rho_{21}(r,t)]^T. \tag{3.1}$$

The superscript T on a vector or a matrix quantity represents the transpose operation. $|\rho(r,t)\rangle\rangle$ corresponds to a state vector in the Liouville space with the basis set $\{|11\rangle\rangle, |22\rangle\rangle, |12\rangle\rangle, |21\rangle\rangle\}$. We use the double angle bracket notations to denote vectors in the Liouville space.[31] The Liouville space vector $|ij\rangle\rangle$ corresponds to the Hilbert space operator $|i\rangle\langle j|$. In terms of the Liouville space language Eq. (2.16) can be written as

$$\frac{\partial}{\partial t}|\rho(r,t)\rangle\rangle = \mathscr{L}_0(r)|\rho(r,t)\rangle\rangle - i\mathscr{W}|\rho(r,t)\rangle\rangle$$

$$-\mathscr{S}(r)|\rho(r,t)\rangle\rangle, \tag{3.2}$$

where

$$\mathscr{L}_0(r) = L_0(r)\mathscr{T}, \tag{3.3}$$

$$\mathscr{W} = \frac{1}{\hbar}\begin{pmatrix} 0 & 0 & -\Delta^* & \Delta \\ 0 & 0 & \Delta^* & -\Delta \\ -\Delta & \Delta & \epsilon_1 - \epsilon_2 & 0 \\ \Delta^* & -\Delta^* & 0 & \epsilon_2 - \epsilon_1 \end{pmatrix}, \tag{3.4}$$

$$\mathscr{S}(r) = \begin{pmatrix} S_1(r) & 0 & 0 & 0 \\ 0 & S_2(r) & 0 & 0 \\ 0 & 0 & \tfrac{1}{2}[S_1(r)+S_2(r)] & 0 \\ 0 & 0 & 0 & \tfrac{1}{2}[S_1(r)+S_2(r)] \end{pmatrix}, \tag{3.5}$$

and $\mathscr{T}$ is the identity operator in the Liouville space. We use the bold script letters to represent operators (or their matrix representations) acting on a state vector in the Liouville space. The reaction rate coefficient given by Eqs. (2.12) and (2.13) is re-expressed as

$$k_f(t) = k_1(t) + k_2(t) = \langle\langle 11|k_f(t)\rangle\rangle + \langle\langle 22|k_f(t)\rangle\rangle, \tag{3.6}$$

where $|k_f(t)\rangle\rangle$ is the reaction rate coefficient vector defined by

$$|k_f(t)\rangle\rangle = \int d\mathbf{r} \ \mathscr{S}(r)|\rho(r,t)\rangle\rangle. \tag{3.7}$$

The formal solution of Eq. (3.2) can be written as

$$|\rho(r,t)\rangle\rangle = \exp[t\mathscr{L}_F(r)]|\rho(r,0)\rangle\rangle$$

$$= \exp[t\mathscr{L}_0(r)]|\rho(r,0)\rangle\rangle - \int_0^t d\tau \, \exp[\tau\mathscr{L}_F(r)]$$

$$\times \mathscr{S}(r)\exp[(t-\tau)\mathscr{L}_0(r)]|\rho(r,0)\rangle\rangle$$

$$- i\int_0^t d\tau \, \exp[\tau\mathscr{L}_F(r)]\mathscr{W}$$

$$\times \exp[(t-\tau)\mathscr{L}_0(r)]|\rho(r,0)\rangle\rangle, \qquad (3.8)$$

where the full evolution operator $\mathscr{L}_F(r)$ is defined by

$$\mathscr{L}_F(r) = \mathscr{L}_0(r) - \mathscr{S}(r) - i\mathscr{W}, \qquad (3.9)$$

and in writing the second equality in Eq. (3.8) we have used the following operator identity,[32]

$$e^{t(M+n)} = e^{tM} + \int_0^t d\tau \, e^{\tau(M+N)} N e^{(t-\tau)M}. \qquad (3.10)$$

We assume that the reactant molecules are distributed in equilibrium at time zero,

$$|\rho(r,0)\rangle\rangle = g(r)|\alpha_0\rangle\rangle, \qquad (3.11)$$

where $g(r)[=e^{-\beta U(r)}]$ is the equilibrium pair correlation between A and B molecules and $|\alpha_0\rangle\rangle$ is the initial state vector representing the quantum state of the statistical mixture of A-B pairs. In writing Eq. (3.11) we have assumed implicitly that the potentials of mean force between A and B molecules are the same irrespective of the quantum state of B. This assumption is a reasonable one if the overall molecular geometries of B are similar in the two states. Since $g(r)$ is the equilibrium pair correlation function, we have $L_0(r)g(r)=0$, and Eq. (3.8) reduces to

$$|\rho(r,t)\rangle\rangle = |\rho(r,0)\rangle\rangle - \int_0^t d\tau \, \exp[\tau\mathscr{L}_F(r)].\mathscr{S}(r)|\rho(r,0)\rangle\rangle$$

$$- i\int_0^t d\tau \, \exp[\tau\mathscr{L}_F(r)]\mathscr{W}|\rho(r,0)\rangle\rangle. \qquad (3.12)$$

We then introduce the propagator matrices

$$\mathscr{G}_F(r,t|r_0) = \exp[t\mathscr{L}_F(r)]\frac{\delta(r-r_0)}{4\pi r_0^2}, \qquad (3.13)$$

$$\mathscr{G}(r,t|r_0) = \exp[t(\mathscr{L}_0(r) - i\mathscr{W})]\frac{\delta(r-r_0)}{4\pi r_0^2}. \qquad (3.14)$$

The full propagator matrix $\mathscr{G}_F(r,t|r_0)$ gives the probability for an A-B pair to move from the spatial separation r_0 to r over a time interval of t under the full dynamic influence arising from thermal diffusive motion, quantum transition, and chemical reaction. On the other hand, the *reaction-free* propagator matrix $\mathscr{G}(r,t|r_0)$ refers to an evolution without the chemical reaction. With Eqs. (3.12)–(3.14) we can recast the expression for the reaction rate coefficient vector in the form

$$|k_f(t)\rangle\rangle = |k_0\rangle\rangle - \int_0^t d\tau |\lambda(\tau)\rangle\rangle - i\int_0^t d\tau |\pi(\tau)\rangle\rangle, \quad (3.15)$$

where the first term on the RHS is the initial rate coefficient vector defined by

$$|k_0\rangle\rangle = \int d\mathbf{r}.\mathscr{S}(r)g(r)|\alpha_0\rangle\rangle, \qquad (3.16)$$

and the rate kernels in the second and third terms are defined by

$$|\lambda(t)\rangle\rangle = \int d\mathbf{r}.\mathscr{S}(r)\int d\mathbf{r}_0 \, \mathscr{G}_F(r,t|r_0).\mathscr{S}(r_0)g(r_0)|\alpha_0\rangle\rangle, \qquad (3.17)$$

$$|\pi(t)\rangle\rangle = \int d\mathbf{r}.\mathscr{S}(r)\int d\mathbf{r}_0 \, \mathscr{G}_F(r,t|r_0)\mathscr{W}g(r_0)|\alpha_0\rangle\rangle. \qquad (3.18)$$

We assume that the reaction occurs when A and B molecules are brought into contact at the separation of $r=\sigma$. Then the reaction sink matrix may be modeled by using the delta function:

$$\mathscr{S}(r) = \frac{\delta(r-\sigma)}{4\pi\sigma^2}.\mathscr{K}, \qquad (3.19)$$

where the intrinsic reactivity matrix $\mathscr{K}$ is defined by

$$\mathscr{K} = \begin{pmatrix} \kappa_1 & 0 & 0 & 0 \\ 0 & \kappa_2 & 0 & 0 \\ 0 & 0 & \bar{\kappa} & 0 \\ 0 & 0 & 0 & \bar{\kappa} \end{pmatrix}. \qquad (3.20)$$

κ_1 and κ_2 are the intrinsic bimolecular rate constants for the reaction of A molecules with B molecules in the quantum states $|1\rangle$ and $|2\rangle$, respectively, and $\bar{\kappa} = (\kappa_1 + \kappa_2)/2$.

Laplace transformation of Eq. (3.15) with Eqs. (3.16)–(3.19) gives

$$|\hat{k}_f(z)\rangle\rangle = g(\sigma)z^{-1}.\mathscr{K}[\mathscr{I} - \hat{\mathscr{G}}_F(\sigma,z|\sigma).\mathscr{K}$$

$$- i.\hat{\mathscr{M}}_F(z)\mathscr{W}]|\alpha_0\rangle\rangle, \qquad (3.21)$$

with the Laplace-transformed quantity denoted as $\hat{f}(z) \equiv \int_0^\infty dt \, f(t)e^{-zt}$. $\hat{\mathscr{M}}_F(z)$ is related to the full propagator matrix:

$$\hat{\mathscr{M}}_F(z) \equiv \int d\mathbf{r}_0 \, y(r_0).\hat{\mathscr{G}}_F(\sigma,z|r_0), \qquad (3.22)$$

where $y(r) \equiv g(r)/g(\sigma)$. Applying the operator identity in Eq. (3.10) to Eqs. (3.13) and (3.14), we can relate the reaction-free propagator matrix to the full propagator matrix as

$$\mathscr{G}_F(r,t|r_0) = \mathscr{G}(r,t|r_0)$$

$$- \int_0^t d\tau \mathscr{G}_F(r,t-\tau|\sigma).\mathscr{K}\mathscr{G}(\sigma,\tau|r_0), \quad (3.23)$$

which in the Laplace domain becomes

$$\hat{\mathscr{G}}_F(r,z|r_0) = \hat{\mathscr{G}}(r,z|r_0) - \hat{\mathscr{G}}_F(r,z|\sigma).\mathscr{K}\hat{\mathscr{G}}(\sigma,z|r_0). \qquad (3.24)$$

From Eq. (3.21), after expressing the full propagator matrix in terms of the reaction-free propagator matrix by using

Eq. (3.24), we obtain a general but still formal expression for the reaction rate coefficient vector in the Laplace domain,

$$|\hat{k}_f(z)\rangle\rangle = g(\sigma)z^{-1}\mathcal{K}[\mathcal{I}+\hat{\mathcal{G}}_\sigma(z)\mathcal{K}]^{-1}$$

$$\times[\mathcal{I}-i\hat{\mathcal{M}}(z)\mathcal{W}]|\alpha_0\rangle\rangle, \tag{3.25}$$

where

$$\hat{\mathcal{M}}(z) \equiv \int d\mathbf{r}_0 \, y(r_0)\hat{\mathcal{G}}(\sigma,z|r_0), \tag{3.26}$$

$$\hat{\mathcal{G}}_\sigma(z) \equiv \hat{\mathcal{G}}(\sigma,z|\sigma). \tag{3.27}$$

Once we get an analytical expression or numerical values of the reaction-free propagator matrix $\hat{\mathcal{G}}(r,z|r_0)$ for a specific reaction model, we can evaluate the time-dependent reaction rate coefficient $k_f(t)$ by inverse Laplace transformation of Eq. (3.25) into the time domain.

Expressions for $\hat{\mathcal{G}}_\sigma(z)$ and $\hat{\mathcal{M}}(z)$ can be obtained as follows. Since $\mathcal{L}_0(r)$ and $\mathcal{W}$ commute with each other we have

$$\mathcal{G}(r,t|r_0) = \exp[t(\mathcal{L}_0(r)-i\mathcal{W})]\frac{\delta(r-r_0)}{4\pi r_0^2}$$

$$= \exp(-i\mathcal{W}t)G_0(r,t|r_0), \tag{3.28}$$

where $G_0(r,t|r_0)$ is the Smoluchowski propagator defined by

$$G_0(r,t|r_0) \equiv e^{tL_0(r)}\frac{\delta(r-r_0)}{4\pi r_0^2}. \tag{3.29}$$

We can obtain the expression for $\exp(-i\mathcal{W}t)$ by diagonalizing the $\mathcal{W}$ matrix:[23]

$$\mathcal{W}_D = \mathcal{R}^+\mathcal{W}\mathcal{R} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \omega & 0 \\ 0 & 0 & 0 & -\omega \end{pmatrix}, \tag{3.30}$$

where the unitary transformation matrix $\mathcal{R}$ is given by

$$\mathcal{R} = \begin{pmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{p}{\sqrt{2}} & \dfrac{q^*}{2} & \dfrac{q}{2} \\ \dfrac{1}{\sqrt{2}} & -\dfrac{p}{\sqrt{2}} & -\dfrac{q^*}{2} & -\dfrac{q}{2} \\ 0 & \dfrac{q}{\sqrt{2}} & -\dfrac{1+p}{2} & \dfrac{q^2}{2(1+p)} \\ 0 & \dfrac{q^*}{\sqrt{2}} & \dfrac{q^{*2}}{2(1+p)} & -\dfrac{1+p}{2} \end{pmatrix}, \tag{3.31}$$

with the molecular parameters defined by

$$\omega \equiv \frac{\sqrt{(\epsilon_1-\epsilon_2)^2+4|\Delta|^2}}{\hbar}, \tag{3.32}$$

$$p \equiv \frac{\epsilon_1-\epsilon_2}{\hbar\omega}, \tag{3.33}$$

$$q \equiv \frac{2\Delta}{\hbar\omega}. \tag{3.34}$$

The transition frequency ω defined in Eq. (3.32) is known as the Rabi frequency. Since we have diagonalized the $\mathcal{W}$ matrix, we can obtain an explicit expression of $\exp(-i\mathcal{W}t)$,

$$\exp(-i\mathcal{W}t) = \mathcal{R}\exp(-i\mathcal{W}_Dt)\mathcal{R}^+$$

$$= \begin{pmatrix} |\phi(t)|^2 & 1-|\phi(t)|^2 & q^*\sin(\omega t/2)\phi(t) & q\sin(\omega t/2)\phi^*(t) \\ 1-|\phi(t)|^2 & |\phi(t)|^2 & -q^*\sin(\omega t/2)\phi(t) & -q\sin(\omega t/2)\phi^*(t) \\ q\sin(\omega t/2)\phi(t) & -q\sin(\omega t/2)\phi(t) & -\phi(t)^2 & q^2\sin(\omega t/2) \\ q^*\sin(\omega t/2)\phi^*(t) & -q^*\sin(\omega t/2)\phi^*(t) & q^{*2}\sin(\omega t/2) & -\phi(t)^{*2} \end{pmatrix}, \tag{3.35}$$

where $\phi(t) \equiv p\sin(\omega t/2)+i\cos(\omega t/2)$.

Since the matrix elements of $\exp(-i\mathcal{W}t)$ are expressed by the linear combinations of 1, $e^{-i\omega t}$, and $e^{i\omega t}$, we can easily obtain from Eq. (3.28) the Laplace transform of the reaction-free propagator matrix, $\hat{\mathcal{G}}(r,z|r_0)$, that is expressed in terms of $\hat{G}_0(r,z|r_0)$, $\hat{G}_0(r,z+i\omega|r_0)$, and $\hat{G}_0(r,z-i\omega|r_0)$. Then the matrix $\hat{\mathcal{M}}(z)$ is calculated from Eq. (3.26), and in turn the reaction rate coefficient from Eq. (3.25).

The initial state of A-B pairs in Eq. (3.11) is considered to be an incoherent superposition of the basis states so that

$$|\alpha_0\rangle\rangle = (l_1,l_2,0,0)^T, \tag{3.36}$$

where l_1 and l_2 are the probabilities that B molecules are in the states $|1\rangle$ and $|2\rangle$, respectively, at $t=0$ and thus have the range $0 \leq l_1,l_2 \leq 1$ with $l_1+l_2=1$. For this general initial condition, we can obtain the analytical expressions for the reaction rate coefficients in the Laplace domain from Eq. (3.25) after carrying out quite lengthy but straightforward matrix manipulations:

$$\hat{k}_n(z) = \frac{\kappa_n g(\sigma)}{2z}\frac{(1+\kappa_m\hat{G}_0)D_1+(l_n-l_m)(1+\kappa_m\hat{G}_0)[(1-C)D_1+CD_3]+C[(\kappa_n-\kappa_m)/(2\bar\kappa)](D_2-D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1+C[(\kappa_1-\kappa_2)^2/(4\bar\kappa)]\hat{G}_0(D_2-D_1)}$$

$$(n=1 \text{ or } 2; \text{ if } n=1, m=2; \text{ else if } n=2, m=1), \tag{3.37}$$

$$\hat{k}_f(z) = \frac{g(\sigma)}{z} \frac{(\bar{\kappa} + \kappa_1 \kappa_2 \hat{G}_0)D_1 + [(l_1 - l_2)(\kappa_1 - \kappa_2)/2][(1-C)D_1 + CD_3] + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})](D_2 - D_1)}{(1 + \kappa_1 \hat{G}_0)(1 + \kappa_2 \hat{G}_0)D_1 + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)}, \tag{3.38}$$

where

$$D_1 \equiv (1 + \bar{\kappa}\hat{G}_+)(1 + \bar{\kappa}\hat{G}_-), \tag{3.39}$$

$$D_2 \equiv \tfrac{1}{2}(1 + \bar{\kappa}\hat{G}_0)(1 + \bar{\kappa}\hat{G}_+) + \tfrac{1}{2}(1 + \bar{\kappa}\hat{G}_0)(1 + \bar{\kappa}\hat{G}_-), \tag{3.40}$$

$$D_3 \equiv \tfrac{1}{2}(1 + \bar{\kappa}\hat{G}_0)(1 + \bar{\kappa}\hat{G}_+)(1 + i\omega\hat{M}_-)$$
$$+ \tfrac{1}{2}(1 + \bar{\kappa}\hat{G}_0)(1 + \bar{\kappa}\hat{G}_-)(1 - i\omega\hat{M}_+). \tag{3.41}$$

We have used the following abbreviated notations for the Smoluchowski propagators,

$$\hat{G}_0 \equiv \hat{G}_0(\sigma, z|\sigma), \tag{3.42}$$

$$\hat{G}_\pm \equiv \hat{G}_0(\sigma, z \pm i\omega|\sigma), \tag{3.43}$$

and $\hat{M}_+$ and $\hat{M}_-$ are defined by

$$\hat{M}_\pm \equiv \int d\mathbf{r}_0 y(r_0)\hat{G}_\pm(\sigma, z \pm i\omega|r_0). \tag{3.44}$$

We have also defined the coupling constant C as

$$C \equiv |q|^2, \tag{3.45}$$

which has the range of $0 \leqslant C \leqslant 1$.

IV. SIMPLE MODEL CASES

An analytical expression for the Smoluchowski propagator $\hat{G}_0(r, z|r_0)$ can be obtained for the following reaction model. The potential of mean force between A and B molecules, $U(r)$, is assumed to be given by

$$U(r) = \begin{cases} \infty & \text{for } 0 \leqslant r < \sigma \\ 0 & \text{for } r \geqslant \sigma \end{cases}. \tag{4.1}$$

The hydrodynamic interaction is neglected so that the relative diffusion coefficient is simply given by the sum of self-diffusion coefficients of A and B molecules:

$$d(r) = D_A + D_B = D. \tag{4.2}$$

Then with the boundary conditions,

$$\left[D\left(\frac{\partial}{\partial r} + \beta \frac{\partial U(r)}{\partial r} \right) \hat{G}(r, z|r_0) \right]_{r=\sigma} = 0, \tag{4.3}$$

$$\lim_{r \to \infty} \hat{G}_0(r, z|r_0) = 0, \tag{4.4}$$

we can readily obtain[33]

$$\hat{G}_0(r, z|r_0)$$
$$= \frac{1}{4\pi D r r_0} \left\{ \frac{1}{2\sqrt{z/D}} (e^{-\sqrt{z/D}|r - r_0|} - e^{-\sqrt{z/D}(r + r_0 - 2\sigma)}) \right.$$
$$\left. + \frac{\sigma}{1 + \sigma\sqrt{z/D}} e^{-\sqrt{z/D}(r + r_0 - 2\sigma)} \right\} \quad (\text{for } r, r_0 \geqslant \sigma), \tag{4.5}$$

where $k_D = 4\pi\sigma D$. When $r = r_0 = \sigma$ the Smoluchowski propagator $\hat{G}_0(r, z|r_0)$ reduces to

$$\hat{G}_0 = \hat{G}_0(\sigma, z|\sigma) = \frac{1}{k_D(1 + \sqrt{t_D z})}, \tag{4.6}$$

where $t_D = \sigma^2/D$ measures the timescale of relative diffusion between A and B molecules. We can also obtain analytical expressions for $\hat{M}_\pm$ given in Eq. (3.44),

$$\hat{M}_\pm = \int d\mathbf{r}_0 \ y(r_0)\hat{G}_0(\sigma, z \pm i\omega|r_0) = \frac{1}{z \pm i\omega}, \tag{4.7}$$

since $y(r_0) = 1$ for $r \geqslant \sigma$.

We can easily confirm that when the two quantum states of B are not coupled to each other (that is, $C = 0$), the reaction rate coefficients given by Eqs. (3.37) and (3.38) reduce to the well known results for the diffusion-influenced reaction between simple hard spheres with the Collins–Kimball boundary condition,[4]

$$\hat{k}_n^{ZC}(z) = l_n \hat{k}_n^0(z), \tag{4.8}$$

$$\hat{k}_f^{ZC}(z) = l_1 \hat{k}_1^0(z) + l_2 \hat{k}_2^0(z), \tag{4.9}$$

where

$$\hat{k}_n^0(z) = \frac{\kappa_n}{z(1 + \kappa_n \hat{G}_0)} = \frac{\kappa_n k_D(1 + \sqrt{t_D z})}{z[\kappa_n + k_D(1 + \sqrt{t_D z})]}. \tag{4.10}$$

The superscript ZC denotes the "zero coupling" case. The Laplace domain expressions for the rate coefficients in Eqs. (4.8) and (4.9) are easily inverted to the time domain,[4,30]

$$k_n^{ZC}(t) = l_n k_n^0(t), \tag{4.11}$$

$$k_f^{ZC}(t) = l_1 k_1^0(t) + l_2 k_2^0(t), \tag{4.12}$$

where

$$k_n^0(t) = \frac{\kappa_n k_D}{\kappa_n + k_D} \left(1 + \frac{\kappa_n}{k_D} \exp(t/t_R)\text{erfc}(\sqrt{t/t_R}) \right). \tag{4.13}$$

Here t_R is the reaction timescale during which the reaction rate coefficients decrease significantly toward the steady-state values, and is defined by

$$t_R = t_D \left(\frac{k_D}{k_D + \kappa_n} \right)^2. \tag{4.14}$$

Rate coefficient expressions in the time domain are also available in the case when the two intrinsic rate constants are equal to each other (that is, $\kappa_1 = \kappa_2 \equiv \kappa$). We have

$$\hat{k}_n^{ER}(z) = l_n \hat{k}^0(z) + (C/4)(l_n - l_m)$$
$$\times [\hat{k}^0(z + i\omega) + \hat{k}^0(z - i\omega) - 2\hat{k}^0(z)], \tag{4.15}$$

$$\hat{k}_f^{ER}(z) = \hat{k}^{(0)}(z). \tag{4.16}$$

The superscript ER denotes the ''equal reactivity'' case. $\hat{k}^0(z)$ is given by the same expression as Eq. (4.10) with κ_n replaced by κ. Equations (4.15) and (4.16) are easily inverted to give the time-dependent reaction rate coefficients,

$$k_n^{ER}(t) = k^0(t)[l_n - C(l_n - l_m)\sin^2(\omega t/2)], \tag{4.17}$$

$$k_f^{ER}(t) = k^0(t). \tag{4.18}$$

In this equal reactivity case we notice that the reaction rate coefficient for each state of B oscillates in time with the amplitude that is proportional to the coupling constant and the difference in the initial populations in the two states. On the other hand, the total reaction rate coefficient given by Eq. (4.18) does not show an oscillatory behavior. In the reaction with an A molecule it dose not matter whether the B molecule is in the state $|1\rangle$ or in the state $|2\rangle$ since the intrinsic rate constants are the same in the two states. However, if κ_1 and κ_2 differ from each other, the overall rate coefficient $k_f(t)$ will also show an oscillatory behavior.

When the quantum-mechanical transitions between the two internal states of B occur very fast, we can also obtain analytical expressions for the reaction rate coefficients in the time domain. In the large-frequency limit such that $\omega \gg z$ and t_D^{-1}, the reaction rate coefficient in the Laplace domain in Eqs. (3.37)–(3.41) becomes

$$\hat{k}_n^{LF}(z) = \frac{\kappa_n}{4} \left[\left(\frac{a_+^n}{\kappa_+} \right) \hat{k}_+^0(z) + \left(\frac{a_-^n}{\kappa_-} \right) \hat{k}_-^0(z) \right], \tag{4.19}$$

$$\hat{k}_f^{LF}(z) = \left(\frac{1}{2} + \frac{|p|}{2} \frac{(l_1 - l_2)(\kappa_1 - \kappa_2)}{|\kappa_1 - \kappa_2|} \right) \hat{k}_+^0(z)$$
$$+ \left(\frac{1}{2} - \frac{|p|}{2} \frac{(l_1 - l_2)(\kappa_1 - \kappa_2)}{|\kappa_1 - \kappa_2|} \right) \hat{k}_-^0(z), \tag{4.20}$$

where

$$\kappa_\pm = \bar{\kappa} \pm \frac{|p||\kappa_1 - \kappa_2|}{2}, \tag{4.21}$$

$$a_\pm^n = \left(|p| \pm \frac{\kappa_n - \kappa_m}{|\kappa_n - \kappa_m|} \right) \left((l_n - l_m)|p| \pm \frac{\kappa_n - \kappa_m}{|\kappa_n - \kappa_m|} \right), \tag{4.22}$$

and $\hat{k}_\pm^0(z)$ are given by the same expression as Eq. (4.10) with κ_n replaced by $\kappa_\pm$. The superscript LF denotes the ''large frequency'' case. Equations (4.19) and (4.20) can be inverted to the time domain. Except for very short times, that is, for $t > \omega^{-1}$ we have

$$k_n^{LF}(t) = \frac{\kappa_n}{4} \left[\left(\frac{a_+^n}{\kappa_+} \right) k_+^0(t) + \left(\frac{a_-^n}{\kappa_-} \right) k_-^0(t) \right], \tag{4.23}$$

$$k_f^{LF}(t) = \left(\frac{1}{2} + \frac{|p|}{2} \frac{(l_1 - l_2)(\kappa_1 - \kappa_2)}{|\kappa_1 - \kappa_2|} \right) k_+^0(t)$$
$$+ \left(\frac{1}{2} - \frac{|p|}{2} \frac{(l_1 - l_2)(\kappa_1 - \kappa_2)}{|\kappa_1 - \kappa_2|} \right) k_-^0(t). \tag{4.24}$$

The structure of Eq. (4.24) reveals that when the Rabi frequency becomes very large, the two reaction channels between A and B molecules are completely mixed to give two new apparent reaction channels characterized by two rate constants, κ_+ and κ_-. When $\epsilon_1 = \epsilon_2$ so that $p = 0$, the reaction rate coefficients in Eqs. (4.23) and (4.24) become independent of the initial conditions and are given by

$$k_n^{LF}(t) = \left(\frac{\kappa_n}{\kappa_1 + \kappa_2} \right) \bar{k}^0(t), \tag{4.25}$$

$$k_f^{LF}(t) = \bar{k}^0(t) \quad (\text{for } t > \omega^{-1}), \tag{4.26}$$

where $\bar{k}^0(t)$ is given by the same expression as Eq. (4.10) with κ_n replaced by $\bar{\kappa}$.

V. TWO REPRESENTATIVE INITIAL CONDITIONS

A. Symmetric initial condition

Consider a reaction system where B molecules are distributed in equilibrium. We assume that the two diabatic states of B, $|1\rangle$ and $|2\rangle$, have the same energies. At $t = 0$, A molecules are sensitized on a sudden (e.g., by photoexcitation) and start to react with B molecules. Then the appropriate initial condition is

$$|\alpha_0^S\rangle\rangle = (1/2, 1/2, 0, 0)^T = \tfrac{1}{2}(|11\rangle\rangle + |22\rangle\rangle). \tag{5.1}$$

The superscript S represents a quantity relevant to this symmetric initial condition.

Since $\epsilon_1 = \epsilon_2$, we have $C = 1$. We also have $\mathcal{W}|\alpha_0^S\rangle \gg 0$, which says that quantum-mechanical evolution between the two states $|1\rangle$ and $|2\rangle$ is stationary. By substituting $l_1 = l_2 = 1/2$ and $C = 1$ into Eqs. (3.37) and (3.38), we obtain

$$\hat{k}_n^S(z) = \frac{\kappa_n}{2z} \frac{(1+\kappa_m\hat{G}_0)D_1 + [(\kappa_n - \kappa_m)/(2\bar{\kappa})](D_2 - D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1 + [(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)},$$ (5.2)

$$\hat{k}_f^S(z) = \frac{1}{z} \frac{(\bar{\kappa} + \kappa_1\kappa_2\hat{G}_0)D_1 + [(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})](D_2 - D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1 + [(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)},$$ (5.3)

$g(\sigma)$ has been set to one.

The usual experimental observables would be the time profiles of the concentrations of reaction products, $P_1(t)$ and $P_2(t)$, formed by the reaction of A molecules with B molecules in the states $|1\rangle$ and $|2\rangle$, respectively, rather than the time-dependent reaction rate coefficients. The rate of formation of each product is given by

$$\frac{dP_1(t)}{dt} = k_1(t)[A][B],$$ (5.4)

$$\frac{dP_2(t)}{dt} = k_2(t)[A][B].$$ (5.5)

In the symmetric initial condition case under consideration, it is expected that the concentration of reactive A molecules created at time zero is much smaller than that of B molecules. In this pseudo-first-order case the concentration of B molecules maintains a constant value C_B during the course of reaction, and when the reaction has gone to completion the total concentration of the products [that is, the sum of $P_1(t)$ and $P_2(t)$] will reach the initial concentration of reactive A molecules, denoted as A_0. The rate equations, Eqs. (2.11), (5.4), and (5.5), are then easily integrated to give the product yields $X_1^S(t)$ and $X_2^S(t)$,

$$X_1^S(t) \equiv \frac{P_1(t)}{A_0}$$

$$= C_B \int_0^t dt_1\, k_1^S(t_1)\exp\left(-C_B\int_0^{t_1} dt_2 k_f^S(t_2)\right),$$ (5.6)

$$X_2^S(t) \equiv \frac{P_2(t)}{A_0}$$

$$= C_B \int_0^t dt_1\, k_2^S(t_1)\exp\left(-C_B\int_0^{t_1} dt_2 k_f^S(t_2)\right).$$ (5.7)

B. Asymmetric initial condition

We now consider a reaction system in which B molecules are produced at time zero exclusively in the state $|1\rangle$ (e.g., by photoexcitation). The B molecules then evolve quantum-mechanically between two states $|1\rangle$ and $|2\rangle$, and react with A molecules. An appropriate initial condition for this kind of experimental situation is

$$|\alpha_0^A\rangle\rangle = (1,0,0,0)^T = |11\rangle\rangle.$$ (5.8)

The superscript A represents a quantity relevant to this asymmetric initial condition. Unlike the symmetric initial condition case, the quantum-mechanical evolution between the two states of B is no longer stationary. By substituting $l_1 = 1$ and $l_2 = 0$ into Eqs. (3.37) and (3.38), we obtain

$$\hat{k}_1^A(z) = \frac{\kappa_1}{2z} \frac{(1+\kappa_2\hat{G}_0)[(2-C)D_1 + CD_3] + C[(\kappa_1 - \kappa_2)/(2\bar{\kappa})](D_2 - D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1 + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)},$$ (5.9)

$$\hat{k}_2^A(z) = \frac{C\kappa_2}{2z} \frac{(1+\kappa_1\hat{G}_0)(D_1 - D_3) + [(\kappa_2 - \kappa_1)/(2\bar{\kappa})](D_2 - D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1 + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)},$$ (5.10)

$$\hat{k}_f^A(z) = \frac{1}{z} \frac{(\bar{\kappa} + \kappa_1\kappa_2\hat{G}_0)D_1 + [(\kappa_1 - \kappa_2)/2][(1-C)D_1 + CD_3] + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})](D_2 - D_1)}{(1+\kappa_1\hat{G}_0)(1+\kappa_2\hat{G}_0)D_1 + C[(\kappa_1 - \kappa_2)^2/(4\bar{\kappa})]\hat{G}_0(D_2 - D_1)}.$$ (5.11)

When there is no coupling between the two states, that is, $C = 0$, the reaction rate via the second quantum state vanishes; that is, $k_2(t) = 0$ in Eq. (5.10).

In the asymmetric initial condition case, we would usually have the situation where $[B] \ll [A] \cong C_A$. Then the product yields, $X_1^A(t)$ and $X_2^A(t)$, are given by

$$X_1^A(t) \equiv \frac{P_1(t)}{B_0}$$

$$= C_A \int_0^t dt_1 \, k_1^A(t_1) \exp\left(-C_A \int_0^{t_1} dt_2 \, k_f^A(t_2)\right),$$

$$(5.12)$$

$$X_2^A(t) \equiv \frac{P_2(t)}{B_0}$$

$$= C_A \int_0^t dt_1 \, k_2^A(t_1) \exp\left(-C_A \int_0^{t_1} dt_2 \, k_f^A(t_2)\right), \quad (5.13)$$

where B_0 is the initial concentration of reactive B molecules.

In both symmetric and asymmetric initial condition cases, we define the total product yield $X(t)$ by the sum of the product yields via two reaction channels,

$$X^{S(A)}(t) \equiv X_1^{S(A)}(t) + X_2^{S(A)}(t). \quad (5.14)$$

VI. NUMERICAL RESULTS AND DISCUSSION

In this section we present the results of numerical calculations of the time-dependent reaction rate coefficients and product yields. We use the inverse Laplace transformation subroutine ''INLAP'' in IMSL[34] to calculate the time-dependent reaction rate coefficients. To calculate the product yields we integrate the rate equations in Eqs. (2.11), (5.4), and (5.5) by using the fourth-order Runge–Kutta integrator.[35] All the results are obtained for the simple case with hard-sphere potential of mean force and negligible hydrodynamic interaction.

Figures 1 and 2 show the results obtained for the symmetric initial condition case. The coupling constant C is set

equal to unity as the two diabatic states are degenerate. In Fig. 1 we investigate the effects of changing the Rabi frequency. The intrinsic rate constants are set to be different in the two reaction channels: $\kappa_1 = 10 k_D$ and $\kappa_2 = k_D$. When the inverse of the Rabi frequency is comparable to the diffusion time scale ($\omega t_D = 10$), we can observe a wiggling behavior of the rate coefficient at short times. However, when the Rabi frequency becomes large ($\omega t_D = 100$) we can hardly observe such wiggling in the rate coefficients. Probably the more important point may be that as the Rabi frequency increases, the rate coefficient $k_1(t)$ for the more reactive state becomes larger while $k_2(t)$ for the less reactive state becomes smaller. Accordingly, as Fig. 1(b) shows, the relative product yield $X_1(t)$ over $X_2(t)$ gets larger for the case with the larger Rabi frequency. This result can be explained qualitatively as follows. As time goes by, the reaction rate coefficients decrease as the pair correlation function between A and B molecules gets depleted as the short distance. This depletion occurs to a larger extent for B molecules in the more reactive state; that is $\rho_{11}(r,t) < \rho_{22}(r,t)$. However, quantum-mechanical transitions between the two internal states of B lead to a net population transfer from the less reactive state to the more reactive state. This population transfer is facilitated with the increase in Rabi frequency. Hence as ω increases, $k_1(t)$ gets larger by taking off $k_2(t)$ and so does the relative product yield $X_1(t)$ over $X_2(t)$. Also, the overall rate coefficient $k_f(t)$ increases with the Rabi frequency. The decrease in ρ_{22} due to internal transitions of B molecules has the same magnitude as the increase in ρ_{11}. Hence $k_f(t)$, given by the weighted average $[\kappa_1 \rho_{11}(\sigma,t) + \kappa_2 \rho_{22}(\sigma,t)]$, gets larger with the increase of ω since $\kappa_1 > \kappa_2$.

Figure 2 shows the effects of disparity in the intrinsic
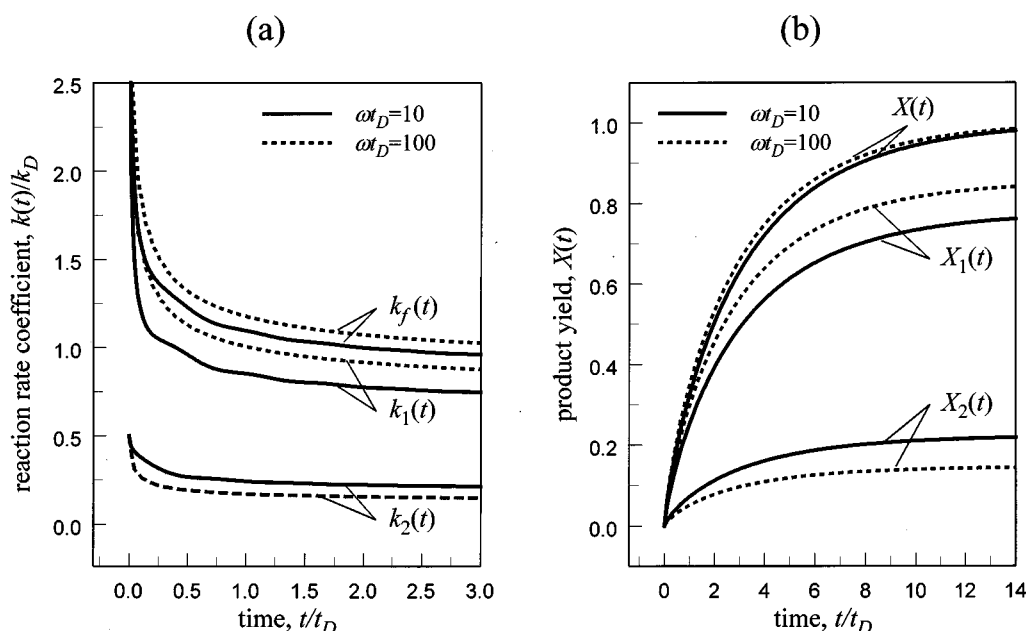

(a)   (b)

FIG. 1. Effects of the Rabi frequency on the time dependence of (a) the reaction rate coefficients and (b) the product yields in the symmetric initial condition case. The coupling constant C is set equal to unity, and the intrinsic rate constants are $\kappa_1 = 10 k_D$ and $\kappa_2 = k_D$. The concentration of B molecules is $\phi_B \equiv \frac{4}{3} \pi \sigma^3 C_B = 0.1$.
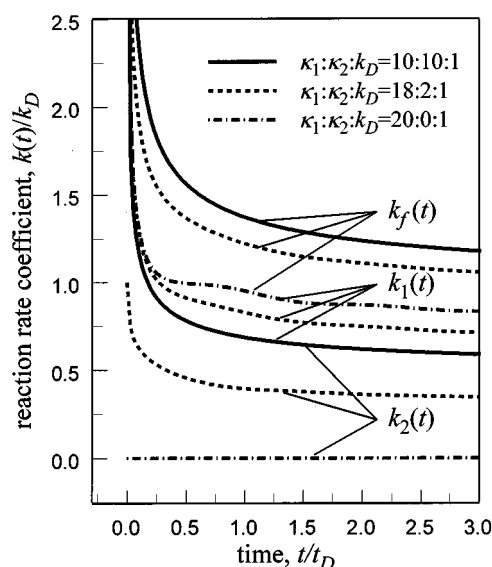
FIG. 2. Effects of the disparity in intrinsic reactivities on the time dependence of the reaction rate coefficients in the symmetric initial condition case. The sum of the intrinsic rate constants are fixed at the value of $20k_D$ in all cases. Values of other parameters are $C=1$, $\omega t_D=5$, and $\phi_B = \frac{4}{3}\pi\sigma^3 C_B = 0.1$.

reactivities in the symmetric initial condition case. The sum of two intrinsic rate constants, κ_1 and κ_2, are kept at the constant value of $20k_D$. The coupling constant C is set equal to unity, and $\omega t_D=5$. When $\kappa_1=\kappa_2=10k_D$, we have $k_1(t)=k_2(t)$ and $k_f(t)=2k_1(t)$, as displayed by the solid curves. On the other hand, when $\kappa_1=20k_D$ and $\kappa_2=0$, $k_f(t)=k_1(t)$, and $k_2(t)=0$ as displayed by the dot-dashed curves.

The dashed curves for the intermediate case with $\kappa_1=18k_D$ and $\kappa_2=2k_D$ lie between the above two limiting cases. Here it should be noted that the overall reaction rate gets larger as the difference in the intrinsic rate constants becomes smaller.

Figures 3 to 6 show the results obtained for the asymmetric initial condition case. The coupling constant C may now have any value between 0 and 1, since $\epsilon_1 \neq \epsilon_2$ in general.

Figure 3 displays the effects of the magnitude of the coupling constant on the time dependence of the reaction rate coefficients and the product yields. The solid curves represent the results for the case with $C=1$ and the dashed curves for the case with $C=0.3$. Values of other parameters used are: $\omega t_D=2$, $\kappa_1=10k_D$, and $\kappa_2=k_D$. At $t=0$, all the reactive B molecules are in the state $|1\rangle$. As the B molecules make transitions back and forth between the two states $|1\rangle$ and $|2\rangle$, the reaction rate coefficient oscillates with the Rabi frequency. The oscillation amplitude gets larger by increasing the coupling constant. Since κ_1 is larger than κ_2, with the increase in the oscillation amplitude, the overall rate coefficient gets smaller and the total product yield goes up more slowly.

When the B molecules are populated exclusively in the state $|1\rangle$ at $t=0$ and κ_1 is ten times as large as κ_2, the product yield via the first reaction channel, $X_1(t)$, is greater than that of the second reaction channel, $X_2(t)$, for all time regions even when $C=1$. However, when κ_2 is ten times as large as κ_1, the situation becomes more complicated as shown in Fig. 4. With the exception that the relative magnitude of κ_1 to κ_2 is reversed, other parameters are the same as in Fig. 3. Again, the reaction rate coefficients oscillate with the Rabi frequency and the oscillation amplitude gets larger

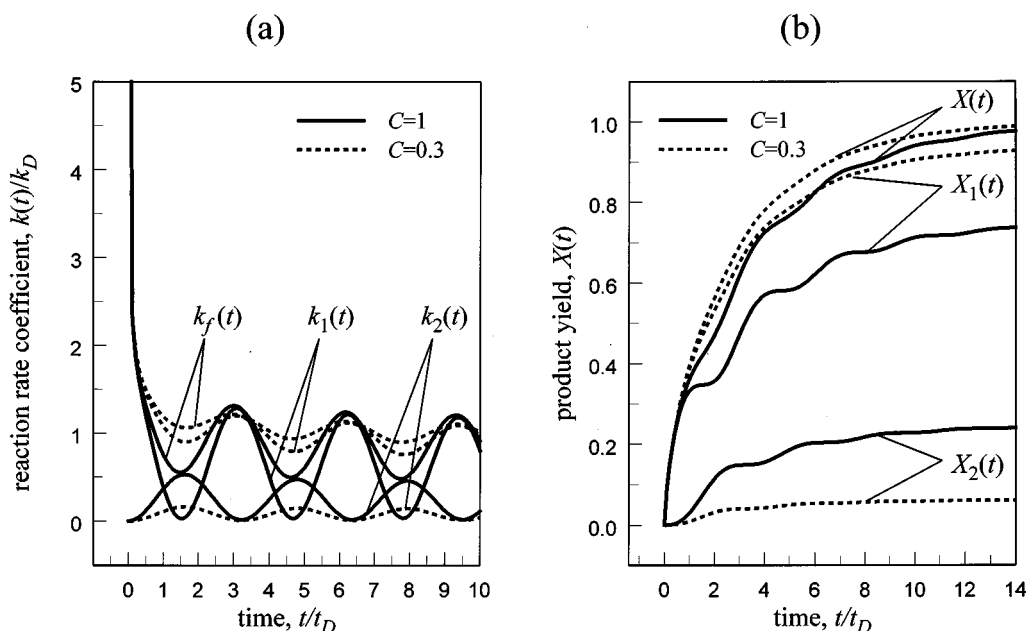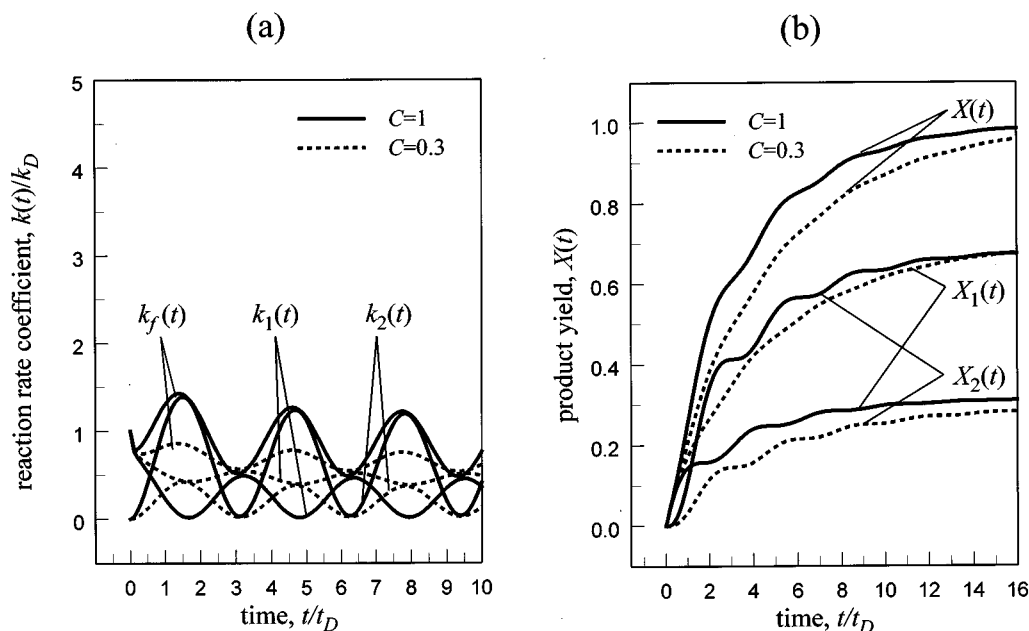<div style="text-align:center">(a)   (b)</div>

FIG. 3. Effects of the coupling constant on the time dependence of (a) the reaction rate coefficients and (b) the product yields in the asymmetric initial condition case. The intrinsic rate constants are $\kappa_1=10k_D$ and $\kappa_2=k_D$, and the Rabi frequency is $\omega t_D=2$. The concentration of A molecules is $\phi_A \equiv \frac{4}{3}\pi\sigma^3 C_A = 0.1$.

(a)

(b)

FIG. 4. Effects of the coupling constant on the time dependence of (a) the reaction rate coefficients and (b) the product yields in the asymmetric initial condition case. The same parameter values as in Fig. 3 are used except that $\kappa_1 = k_D$ and $\kappa_2 = 10k_D$.

with stronger coupling. However, in contrast with the case depicted in Fig. 3, the overall rate coefficient gets larger with the increase in the magnitude of the coupling constant, since a larger fraction of B molecules can make transitions to the more reactive $|2\rangle$ state. As for the relative product yield, $X_1(t)$ may become smaller than $X_2(t)$ as the coupling between the two internal states of B becomes stronger. As shown in Fig. 4(b), when $C = 0.3$ the relative product yield is dominated by the asymmetric initial condition; $X_1(t)$ is

larger than $X_2(t)$ for all time regions. On the other hand, when $C = 1$, the relative product yield is governed by the initial condition only at short times ($t/t_D \lesssim 1$), and eventually $X_2(t)$ gets larger than $X_1(t)$ as B molecules move into the more reactive $|2\rangle$ state.

Figure 5 shows the effects of the Rabi frequency on the product yields in the asymmetric initial condition case. We take $C = 1$, $\kappa_1 = 10k_D$, and $\kappa_2 = k_D$ in Fig. 5(a), and $\kappa_1 = k_D$ and $\kappa_2 = 10k_D$ in Fig. 5(b). When the Rabi frequency is
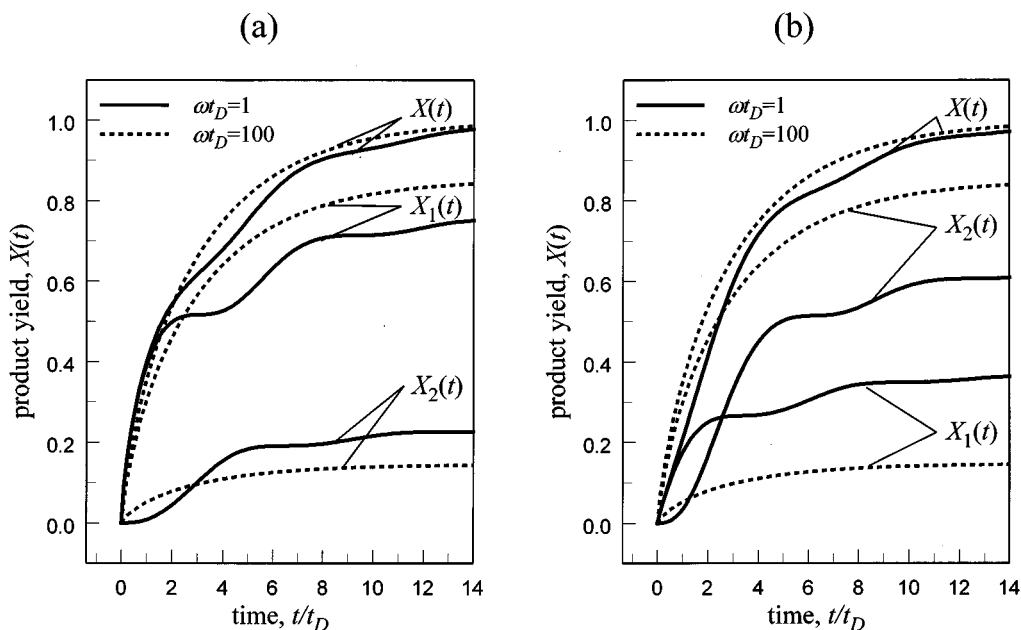
(a)

(b)

FIG. 5. Effects of the Rabi frequency on the product yields in the asymmetric initial condition case. The intrinsic rate constants are $\kappa_1 = 10k_D$ and $\kappa_2 = k_D$ in (a), and $\kappa_1 = k_D$ and $\kappa_2 = 10k_D$ in (b). Values of other parameters are $C = 1$, and $\phi_A = \frac{4}{3}\pi\sigma^3 C_A = 0.1$.
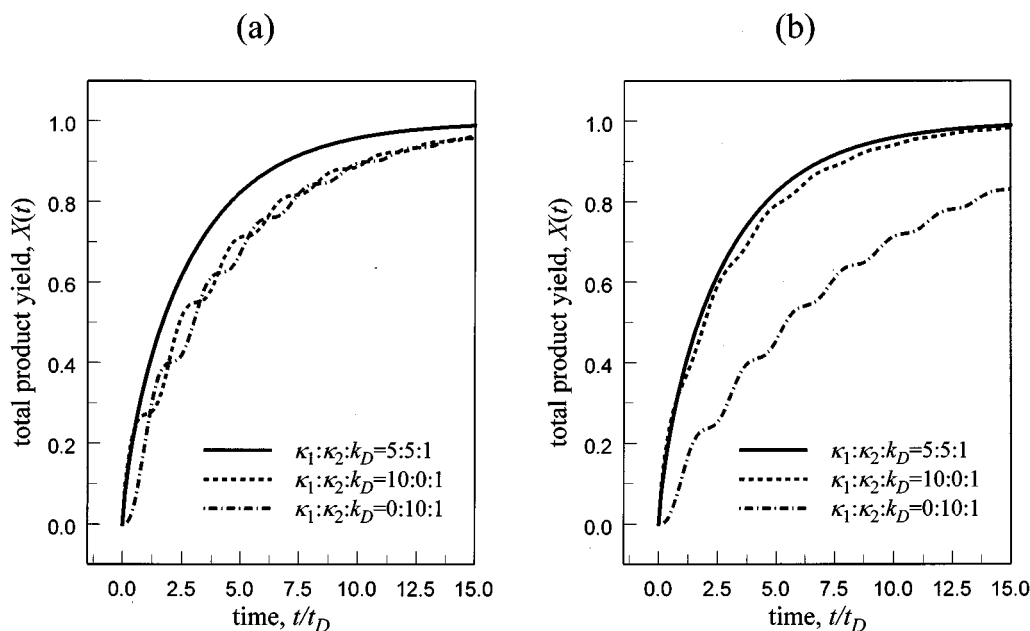
FIG. 6. Effects of the disparity in the intrinsic reactivities on the total product yield in the asymmetric initial condition case. The sum of the intrinsic rate constants are fixed at the value of $10k_D$ in all cases. $C=1$ in (a) and $C=0.5$ in (b). Values of other parameters used are $\omega t_D=3$ and $\phi_A=\frac{4}{3}\pi\sigma^3 C_A=0.1$.

small ($\omega t_D=1$), we can observe a wiggling behavior of the product yield. However, when the Rabi frequency becomes large ($\omega t_D=100$) the product yields increase rather smoothly. When $\kappa_1>\kappa_2$ as in Fig. 5(a) the product yield for the more reactive channel $X_1(t)$ is always larger than that for the less reactive channel $X_2(t)$ for all times, irrespective of the Rabi frequency. However, for the case with $\kappa_1<\kappa_2$ as in Fig. 5(b) the product yield for the more reactive channel $X_2(t)$ may be smaller than that for the less reactive channel $X_1(t)$ at short times due to the initial condition effect. This is more obvious for the case with small ω. Comparing the product yields for the asymmetric initial condition case in Fig. 5 with those for the symmetric initial condition case in Fig. 1, we note that for the large frequency case ($\omega t_D=100$) $X_1(t)$ in Fig. 1(b), $X_1(t)$ in Fig. 5(a), and $X_2(t)$ in Fig. 5(b) coincide with each other for $t>\omega^{-1}$. Similarly, $X_2(t)$ in Fig. 1(b), $X_2(t)$ in Fig. 5(a), and $X_1(t)$ in Fig. 5(b) coincide with each other. The reason for this coincidence is that for the large frequency case the reaction rate coefficients become independent of the initial condition if $p=0$ (that is, when $C=1$), as given by Eq. (4.25). The product yields for reaction channels with the same intrinsic rate constant coincide with each other for $t>\omega^{-1}$.

Finally, we investigate the effects of the disparity in the intrinsic reactivities on the total product yield in the asymmetric initial condition case in Fig. 6. The sum of two intrinsic rate constants, κ_1 and κ_2, are kept at the constant value of $10k_D$. When the coupling constant has the maximum value of unity the total product yield increases most rapidly in the case with $\kappa_1=\kappa_2$ as shown in Fig. 6(a). When either of the two internal states of B is nonreactive (that is, when either κ_1 or κ_2 is zero), the total product yields increase more slowly than for the equal reactivity case, and can be

characterized by the staircaselike increase due to alternation between the reactive and nonreactive states of B. However, when the coupling between the two states has an intermediate value, as in Fig. 6(b), the total product yield for the case with $\kappa_2=0$ just slightly falls behind that for the equal reactivity case. But the total product yield for the case with $\kappa_1=0$ increases much more slowly.

VII. CONCLUDING REMARKS

In this article we have formulated a theory of quantum-mechanically gated diffusion-influenced bimolecular reactions by generalizing the reduced distribution function formalism. The quantum gating mode has been treated within the two-state model. We neglect the dissipation effect arising from the coupling between the gating mode and the surrounding medium.

Analytical expressions for the time-dependent reaction rate coefficients have been obtained in the Laplace transform domain for a general initial condition. Various effects of the quantum-mechanical gating mode on the reaction kinetics have been investigated by calculating the time-dependent rate coefficients and the product yields in the pseudo-first-order cases for two representative initial conditions. In the symmetric initial condition case it has been shown that the overall reaction rate increases with the Rabi frequency, but decreases as the difference between the intrinsic rate constants of the two internal states gets larger. In the asymmetric initial condition case the results vary depending on whether the initially populated internal state is more reactive or not. When the coupling constant and the Rabi frequency, which measure the coupling strength between the two internal states, are small the relative product yields from different

reaction channels are controlled by the initial condition. That is, the reaction channel via the initially populated state dominates. However, when the coupling is very strong, the product branching is biased to the more reactive channel.

We expect that the present theory may be applicable to a wide variety of reactions between two reactants, of which one undergoes a simultaneous intramolecular rearrangement process (e.g., intramolecular charge transfer, changes in the spin state, and so on) that can be modeled as a two-state quantum transition.

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