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Mapping the reaction dynamics in Liouville space onto a reaction coordinate space: A first-principle- based theory

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We have derived here an exact kinetic equation for the time evolution of the probability distribution for a general reaction coordinate space, starting from a multidimensional Liouville equation based on first-principles theory. To make the equation tractable we use two standard approximations, which reduce the exact equation into a Fokker-Planck-type equation with a sink term. As illustrative examples, we consider its application to two important classes of reactions, viz., the electron transfer and diffusion-controlled reactions. The kinetic equations for the reaction coordinates corresponding to these reactions become one dimensional. We also provide a scheme to find the critical value of the reaction coordinate at which the reaction takes place, and also to obtain the initial distribution function in the same space for different experimental situations. In the case of photoinduced electron transfer, we introduce the effect of excitation frequency through the use of suitable initial distribution functions.

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I. INTRODUCTION

Several studies have been concerned with obtaining the transport equations that govern the time evolution of a many-body system starting from first principles. Among them, the most important ones are the works of Zwanzig [1] and Mori [2], which made use of the projection operator technique, first introduced by Zwanzig. In subsequent developments, Garcìa-Colìn and Rio [3,4] have proposed a unified method for deriving the exact kinetic equations governing the time evolution of the dynamical quantities of many-body systems. They have shown that the results obtained by Mori and Zwanzig are the special cases of this scheme, which depend only on how the system was prepared at an initial time ($t = 0$). In their theory, they have proposed a generalized projection operator, which yielded exactly the generalized kinetic equations of the coarse-grained or mesoscopic distribution function $g(a,t)$ for various quantities, namely, the hypershell defined in the phase space (Γ) by the numerical values $\{a\}$ of the function $\{A(\Gamma)\}$. Although the exact generalized kinetic equation is used for extracting applications, and most of them have been concerned with physical processes, as yet no attempt has been made to derive the generalized kinetic equation [5] for describing reactions in solution. Dynamical processes in the condensed phase such as electron transfer (ET) reactions, diffusive escape from potential wells, activated barrier crossing, nonequilibrium solvation, etc., are of immense and longstanding importance in various frontier areas of research in physics, chemistry, and biology. A theoretical description of these phenomena is, however, severely hindered by the multidimensional nature of the collective motion involved. The objective of the present work is to bypass these difficulties by developing alternative simpler approaches for describing reaction dynamics in condensed phase.

II. THEORETICAL FORMALISM

In the case of nonequilibrium processes, initially the system is prepared away from the equilibrium state, and in subsequent times, relaxation of the molecules in a downhill potential brings the system to the equilibrium state. For a given system, the dynamics of relaxation depends on the state of initial preparation. Once the system reaches the equilibrium state, it remains there forever. However, in the case of chemical reactions in solution, depending on experimental situations, the system can undergo reactions starting with equilibrium or nonequilibrium initial conditions. Even a system initially at equilibrium, in subsequent time, no longer remains in the equilibrium state owing to chemical reaction. In the cases of nonequilibrium initial conditions, the system is initially in a multidimensional reactant potential well, and owing to diffusion of phase-space coordinates Γ, the system is brought to the critical configuration $A(\Gamma^*) = a^*$, when the reaction does take place with an intrinsic rate constant k. However, in the case of initial equilibrium conditions, thermal fluctuation first brings the system to the critical configuration characterized by $A(\Gamma^*) = a^*$ and then the reaction takes place. The modified Liouville equation for the reactive system can be written as

$$\frac{\partial \rho(\Gamma,t)}{\partial t} = -[iL + k\delta(A(\Gamma) - a^*)]\rho(\Gamma,t), \tag{1}$$

where L represents the Liouville operator and $\rho(\Gamma,t)$ is the probability density defined in Γ space at time t. For most of the reactions, the phase-space function $A(\Gamma)$ is a function of the geometrical coordinates. However, in the case of energy-diffusion-controlled reactions, the total Hamiltonian H (the function of phase-space coordinates) of the diffusing particle is considered to be $A(\Gamma)$ [6]. In this case, the particle moves with a certain energy ($H = E$) in the potential well, and eventually through thermal fluctuations, the particle energy reaches the barrier energy (E_b) when it escapes. In this case, one has $a^* = E_b$. However, to make our theory more general, here

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we consider a general phase-space function $A(\Gamma)$. The formal solution of Eq. (1) can be written as

$$\rho(\Gamma,t) = e^{-i\tilde{L}t}\rho(\Gamma,0), \tag{2}$$

where $\tilde{L} = L - ik\delta\,[A(\Gamma) - a^*]$ and $\rho(\Gamma,0)$ is the initial probability distribution. The average value $\alpha(t)$ of the phase-space function $A(\Gamma)$ is defined as

$$\alpha(t) = \int d\Gamma\, \rho(\Gamma,t)A(\Gamma). \tag{3}$$

Thus, if one knows the time evolution of $\rho(\Gamma,t)$, one can, in principle, find $\alpha(t)$. Alternatively, one can evaluate $\alpha(t)$ by using the equation

$$\alpha(t) = \int d\Gamma\, \rho(\Gamma,0)A(\Gamma,t), \tag{4}$$

where $A(\Gamma,t) = e^{i\tilde{L}^\dagger t}A(\Gamma,0)$ and $\tilde{L}^\dagger = L + ik\delta\,[A(\Gamma) - a^*]$, with $\tilde{L}^\dagger$ as the Hermitian adjoint of $\tilde{L}$. One of the quantities of interest is $p(t)$, which is the probability of finding the system in the reactant well at time t and is defined as

$$p(t) = \int d\Gamma\, \rho(\Gamma,t). \tag{5}$$

Here the reaction takes place when $A(\Gamma)$ reaches a critical value a^*, and hence it is convenient to find the distribution $g(a,t)$ of the phase-space function $A(\Gamma)$ to have the numerical value a at time t, which is defined as

$$g(a,t) = \int d\Gamma\, \rho(\Gamma,t)G(a,0), \tag{6}$$

where $G(a,0) = \delta\,[A(\Gamma) - a]$. Alternatively, one can define the same quantity as

$$g(a,t) = \int d\Gamma\, \rho(\Gamma,0)G(a,t), \tag{7}$$

where $G(a,t) = e^{i\tilde{L}^\dagger t}G(a,0)$. Now $p(t)$ can be written in terms of $g(a,t)$ as

$$p(t) = \int da\, g(a,t). \tag{8}$$

In most of the cases, the a space corresponds to a much lower dimension as compared to the Γ space. This leads to much simplification in the evaluation of $p(t)$ through Eq. (8), in comparison to the same through Eq. (5), which involves a multidimensional integral. Thus, it is of great interest to obtain a kinetic equation for $g(a,t)$.

We start by defining the Hilbert space $H_g(\omega/\Gamma)$ through the inner product

$$(A,B) = \int d\Gamma\, \omega(\Gamma)A(\Gamma)B^*(\Gamma), \tag{9}$$

where $\omega(\Gamma)$ is the metric of the space, satisfying $iL\omega(\Gamma) = 0$. Now, by writing $\rho(\Gamma,0)$ as $\omega(\Gamma)\nu(\Gamma,0)$ in Eq. (2) and by using $iL\omega(\Gamma) = 0$, one can show that $\rho(\Gamma,t) = \omega(\Gamma)e^{-i\tilde{L}t}\nu(\Gamma,0) = \omega(\Gamma)\nu(\Gamma,t)$, where

$$\nu(\Gamma,t) = e^{-i\tilde{L}t}\nu(\Gamma,0). \tag{10}$$

By using $iL\omega(\Gamma) = 0$, one can also show that $\tilde{L}$ satisfies the property

$$(A(\Gamma),\tilde{L}B(\Gamma)) = (\tilde{L}^\dagger A(\Gamma),B(\Gamma)). \tag{11}$$

Now, to obtain the relevant kinetic equations, we define the generalized projection operator as defined by Garcìa-Colìn and Rio [3], which projects a phase-space function belonging to $H_g(\omega/\Gamma)$ onto the Hilbert space spanned by $G(b,0)$ (with $b \in \mathbb{R}$). The latter space is defined as $H_G(\omega/\Gamma)$ and the projection operator is written as

$$P_G \equiv \int db \frac{(\cdots,G(b,0))}{[G(b,0)]}G(b,0), \tag{12}$$

where $[G(b,0)] = \int d\Gamma\omega(\Gamma)G(b,0)$. We also note the following properties, which will be used in the subsequent discussions repeatedly, viz.,

$$(G(a,0),G(b,0)) = [G(b,0)]\delta(a-b), \tag{13}$$

$$P_G^2 = P_G, \tag{14}$$

$$P_G G(a,0) = G(a,0), \tag{15}$$

$$(A,P_G B) = (P_G A,B). \tag{16}$$

Here, it is clear that as all the projection operators, P_G is also idempotent and Hermitian. Now, before deriving the kinetic equation for $g(a,t)$, we write Eq. (6) in the following form:

$$g(a,t) = (G(a,t),\nu(\Gamma,0)), \tag{17}$$

and split $G(a,t)$ into two parts, one lying in $H_G(\omega/\Gamma)$ and the other lying in the orthogonal space, as follows:

$$\begin{aligned} G(a,t) &= P_G G(a,t) + (1-P_G)G(a,t) \\ &= \int db\, C(a,t/b)G(b,0) + (1-P_G)G(a,t), \end{aligned} \tag{18a}$$

where

$$C(a,t/b) = \frac{(G(a,t),G(b,0))}{[G(b,0)]}. \tag{18b}$$

Now we shall first derive a kinetic equation for $C(a,t/b)$ as follows:

$$\begin{aligned} \frac{dC(a,t/b)}{dt} &= \frac{\left(\frac{dG(a,t)}{dt},G(b,0)\right)}{[G(b,0)]} \\ &= \frac{(i\tilde{L}^\dagger G(a,t),G(b,0))}{[G(b,0)]} \\ &= -\frac{(G(a,t),i\tilde{L}G(b,0))}{[G(b,0)]}. \end{aligned} \tag{19}$$

Again we split $i\tilde{L}G(b,0)$ into two parts: one lying in $H_G(\omega/\Gamma)$ and the other lying in the orthogonal space, as follows:

$$\begin{aligned} i\tilde{L}G(b,0) &= P_G i\tilde{L}G(b,0) + (1-P_G)i\tilde{L}G(b,0) \\ &= P_G[iLG(b,0)] + P_G[kG(a^*,0)G(b,0)] \\ &\quad + (1-P_G)i\tilde{L}G(b,0). \end{aligned} \tag{20}$$

The first term on the right-hand side can be expressed as

$$\begin{aligned} P_G[iLG(b,0)] &= \int dc \frac{(iLG(b,0),G(c,0))}{[G(c,0)]}G(c,0) \\ &= \int dc\, i\Omega(b,c)G(c,0), \end{aligned} \tag{21a}$$

where the frequency $i\Omega(b,c)$ is defined as

$$i\Omega(b,c) = \frac{(iLG(b,0),G(c,0))}{[G(c,0)]}. \tag{21b}$$

Again, the second term of the right-hand side of Eq. (20) can be simplified as follows:

$$\begin{aligned}
&P_G(kG(a^*,0)G(b,0))\\
&\quad= \int dc\frac{(kG(a^*,0)G(b,0),G(c,0))}{[G(c,0)]}G(c,0)\\
&\quad= \int dc\frac{k\delta(a^*-b)\delta(b-c)[G(c,0)]}{[G(c,0)]}G(c,0)\\
&\quad= k\delta(a^*-b)G(b,0).
\end{aligned} \tag{22}$$

Combining Eqs. (19)–(22), we finally obtain

$$\begin{aligned}
&\frac{dC(a,t/b)}{dt}\\
&\quad= \int dc\frac{i[\Omega(b,c)]^*[G(c,0)]}{[G(b,0)]}C(a,t/c) - k\delta(a^*-b)\\
&\qquad\times C(a,t/b) - \frac{(G(a,t),(1-P_G)i\tilde{L}G(b,0))}{[G(b,0)]}.
\end{aligned} \tag{23}$$

Now, we calculate the last term of the right-hand side as follows:

$$\begin{aligned}
&\frac{(G(a,t),(1-P_G)i\tilde{L}G(b,0))}{[G(b,0)]}\\
&\quad= \frac{(G(a,t),(1-P_G)^2i\tilde{L}G(b,0))}{[G(b,0)]}\\
&\quad= \frac{((1-P_G)G(a,t),(1-P_G)i\tilde{L}G(b,0))}{[G(b,0)]}.
\end{aligned} \tag{24}$$

It can be shown easily that

$$(1-P_G)i\tilde{L}G(b,0) = (1-P_G)iLG(b,0), \tag{25a}$$

whereas $(1-P_G)G(a,t)$ can be expressed in terms of the equation

$$\begin{aligned}
&\frac{d}{dt}(1-P_G)G(a,t)\\
&\quad= (1-P_G)iLG(a,t) - k(1-P_G)[G(a^*,0)G(a,t)].
\end{aligned} \tag{25b}$$

Now, to calculate the last term of the above expression we consider the result

$$\begin{aligned}
P_G[G(a^*,0)G(a,t)] &= \int dc\frac{(G(a^*,0)G(a,t),G(c,0))}{[G(c,0)]}G(c,0)\\
&= \int dc\,\delta(c-a^*)C(a,t/c)G(c,0)\\
&= C(a,t/a^*)G(a^*,0).
\end{aligned} \tag{26}$$

Hence, one has

$$\begin{aligned}
&k(1-P_G)[G(a^*,0)G(a,t)]\\
&\quad= kG(a^*,0)G(a,t) - kC(a,t/a^*)G(a^*,0)\\
&\quad= D_1(a,t) - D_2(a,t),
\end{aligned} \tag{27a}$$

where

$$D_1(a,t) = kG(a^*,0)G(a,t), \tag{27b}$$

$$D_2(a,t) = kC(a,t/a^*)G(a^*,0). \tag{27c}$$

Finally we obtain

$$\begin{aligned}
&\frac{d}{dt}(1-P_G)G(a,t)\\
&\quad= (1-P_G)iLG(a,t) - [D_1(a,t) - D_2(a,t)]\\
&\quad= (1-P_G)iL(1-P_G)G(a,t) + (1-P_G)iLP_GG(a,t)\\
&\qquad- [D_1(a,t) - D_2(a,t)].
\end{aligned} \tag{28}$$

On solving Eq. (28), we obtain

$$\begin{aligned}
&(1-P_G)G(a,t)\\
&\quad= \int dc\int_0^t ds\,C(a,t-s/c)F(c,s)\\
&\qquad- \int_0^t ds\,U(s)\{[D_1(a,t-s) - D_2(a,t-s)]\},
\end{aligned} \tag{29}$$

where the random force $F(c,t)$ is defined as

$$F(c,t) \equiv U(t)\,[(1-P_G)iLG(c,0)]\,, \tag{30}$$

with $U(t) = \exp[(1-P_G)iLt]$.

Combining Eqs. (24), (25), (29), and (30), we obtain

$$\begin{aligned}
&\frac{((1-P_G)G(a,t),F(b,0))}{[G(b,0)]}\\
&\quad= \frac{\left(\left[\int dc\int_0^t ds\,C(a,t-s/c)F(c,s)\right],F(b,0)\right)}{[G(b,0)]}\\
&\qquad-\frac{\left(\int_0^t ds\,U(s)\{[D_1(a,t-s) - D_2(a,t-s)]\},F(b,0)\right)}{[G(b,0)]}\\
&\quad= \int dc\int_0^t ds\,C(a,t-s/c)\frac{(F(c,s),F(b,0))}{[G(b,0)]}\\
&\qquad- M_F^b\left(\int_0^t ds\,U(s)\{[D_1(a,t-s) - D_2(a,t-s)]\}\right),
\end{aligned} \tag{31}$$

where we have used the following definitions:

$$M_F^bf(\Gamma) = \frac{(f(\Gamma),F(b,0))}{[G(b,0)]}, \tag{32}$$

$$K(c,b,s) = \frac{(F(c,s),F(b,0))}{[G(b,0)]}. \tag{33}$$

Thus we see that $K(c,b,s) = M_F^b[F(c,s)]$.

Now, by using Eqs. (31) and (33), we ultimately obtain the kinetic equation for the correlation function $C(a,t/b)$ as

$$\begin{aligned}
&\frac{dC(a,t/b)}{dt}\\
&\quad= \int dc\,C(a,t/c)i\Omega(c,b) - k\delta(a^*-b)C(a,t/b)\\
&\qquad- \int dc\int_0^t ds\,C(a,t-s/c)K(c,b,s)\\
&\qquad+ M_F^b\left(\int_0^t ds\,U(s)\{[D_1(a,t-s) - D_2(a,t-s)]\}\right).
\end{aligned} \tag{34}$$

Now, by combining Eqs. (18) and (29), one obtains

$$\begin{aligned}G(a,t) = {} & \int db\, C(a,t/b)G(b,0) \\ & + \int db \int_0^t ds C(a,t-s/b)F(b,s) - \int_0^t ds\, U(s) \\ & \times \{[D_1(a,t-s) - D_2(a,t-s)]\},\end{aligned} \tag{35}$$

which, on Laplace transformation, leads to the result

$$\begin{aligned}\hat{G}(a,\varepsilon) = {} & \int db\, \hat{C}(a,\varepsilon/b)G(b,0) \\ & + \int db\, \hat{C}(a,\varepsilon/b)\hat{F}(b,\varepsilon) \\ & - \hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\},\end{aligned} \tag{36}$$

where the Laplace transform $\hat{f}(\varepsilon)$ is defined as $\hat{f}(\varepsilon) = \int_0^\infty f(t)e^{-\varepsilon t}\, dt$. Now, by taking the Laplace transform of Eq. (34) and, after proper rearrangement, one has

$$\begin{aligned}& \delta(a-b) + M_F^b(\hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\}) \\ & = \int dc\, \hat{C}(a,\varepsilon/c)[-i\Omega(c,b) + k\delta(a^* - c)\delta(c-b) \\ & \quad + \hat{K}(c,b,\varepsilon) + \varepsilon\delta(c-b)] \\ & = \int dc\, \hat{C}(a,\varepsilon/c)\hat{C}_g^{-1}(c,\varepsilon/b),\end{aligned} \tag{37}$$

where

$$\begin{aligned}\hat{C}_g^{-1}(c,\varepsilon/b) = {} & [-i\Omega(c,b) + k\delta(a^* - c)\delta(c-b) \\ & + \hat{K}(c,b,\varepsilon) + \varepsilon\delta(c-b)].\end{aligned}$$

Now we multiply $\hat{G}(a,\varepsilon)$ with $\hat{C}_g^{-1}(c,\varepsilon/a)$ and integrate over a to obtain

$$\begin{aligned}& \int da \hat{C}_g^{-1}(c,\varepsilon/a)\hat{G}(a,\varepsilon) \\ & = \int da[-i\Omega(c,a) + k\delta(a^* - c)\delta(c-a) \\ & \quad + \hat{K}(c,a,\varepsilon) + \varepsilon\delta(c-a)]\hat{G}(a,\varepsilon) \\ & = \left\{\int da[-i\Omega(c,a) + \hat{K}(c,a,\varepsilon)]\hat{G}(a,\varepsilon)\right\} \\ & \quad + k\delta(a^* - c)\hat{G}(c,\varepsilon) + \varepsilon\hat{G}(c,\varepsilon) \\ & = \int da \int db\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{C}(a,\varepsilon/b)[G(b,0) + \hat{F}(b,\varepsilon)] \\ & \quad - \int da\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\},\end{aligned} \tag{38}$$

where we have made use of Eq. (36). Equation (38) can be simplified further to obtain

$$\begin{aligned}& \int da\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{G}(a,\varepsilon) \\ & = \int db[\delta(c-b) + M_F^b(\hat{U}(\varepsilon)\{[\hat{D}_1(c,\varepsilon) - \hat{D}_2(c,\varepsilon)]\})] \\ & \quad \times [G(b,0) + \hat{F}(b,\varepsilon)] - \int da\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{U}(\varepsilon) \\ & \quad \times \{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\} \\ & = G(c,0) + \hat{F}(c,\varepsilon) + \int db\, M_F^b(\hat{U}(\varepsilon)\{[\hat{D}_1(c,\varepsilon) \\ & \quad - \hat{D}_2(c,\varepsilon)]\})[G(b,0) + \hat{F}(b,\varepsilon)] \\ & \quad - \int da\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\},\end{aligned} \tag{39}$$

where we have used the result $\int dc\, \hat{C}(a,\varepsilon/c)\hat{C}_g^{-1}(c,\varepsilon/b) = \delta(a-b) + M_F^b(\hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\})$.

By equating Eqs. (38) and (39), and after some rearrangement, we obtain

$$\begin{aligned}& k\delta(a^* - c)\hat{G}(c,\varepsilon) + [\varepsilon\hat{G}(c,\varepsilon) - G(c,0)] \\ & = \left\{\int da[i\Omega(c,a) - \hat{K}(c,a,\varepsilon)]\hat{G}(a,\varepsilon)\right\} + \hat{F}(c,\varepsilon) \\ & \quad + \int db M_F^b(\hat{U}(\varepsilon)\{[\hat{D}_1(c,\varepsilon) - \hat{D}_2(c,\varepsilon)]\}) \\ & \quad \times [G(b,0) + \hat{F}(b,\varepsilon)] \\ & \quad - \int da\, \hat{C}_g^{-1}(c,\varepsilon/a)\hat{U}(\varepsilon)\{[\hat{D}_1(a,\varepsilon) - \hat{D}_2(a,\varepsilon)]\},\end{aligned} \tag{40}$$

which, on inverse Laplace transformation, leads to

$$\begin{aligned}& \frac{dG(c,t)}{dt} + k\delta(a^* - c)G(c,t) \\ & = \int da[i\Omega(c,a)]G(a,t) - \int da \int_0^t ds K(c,a,s)G(a,t-s) \\ & \quad + F(c,t) + \int db \int_0^t ds\, M_F^b(U(s)\{[D_1(c,t-s) \\ & \quad - D_2(c,t-s)]\})G(b,0) + \int db \int_0^t ds\, F(b,t-s)M_F^b \\ & \quad \times \left\{\int_0^s dr\, U(s-r)[D_1(c,r) - D_2(c,r)]\right\} \\ & \quad - \int da \int_0^t ds\, \tilde{C}_g^{-1}(c,t-s/a) \int_0^s dr\, U(s-r) \\ & \quad \times \{[D_1(a,r) - D_2(a,r)]\},\end{aligned} \tag{41}$$

where $\tilde{C}_g^{-1}(a,t/b)$ is the inverse Laplace transform of $\hat{C}_g^{-1}(a,\varepsilon/b)$. Equation (41) can be rewritten as

$$\begin{aligned}\frac{dG(a,t)}{dt} = {} & Z(a,t)G(a,t) - k\delta(a^* - a)G(a,t) \\ & + F(a,t) + E(a,t),\end{aligned} \tag{42}$$

where $Z(a,t)$, which represents the Zwanzig operator, is defined as

$$\begin{aligned}Z(a,t)f(a,t) = {} & \int dc\, [i\Omega(a,c)]\, f(c,t) \\ & - \int dc \int_0^t ds\, K(a,c,s)f(c,t-s),\end{aligned} \tag{43a}$$

and $E(a,t)$ is given by

$$\begin{aligned}E(a,t) = {} & + \int db \int_0^t ds\, M_F^b(U(s) \\ & \times \{[D_1(a,t-s) - D_2(a,t-s)]\}) \\ & \times G(b,0) + \int db \int_0^t ds\, F(b,t-s)M_F^b\end{aligned}$$

$$\times \left\{ \int_0^s dr\, U(s-r)[D_1(a,r) - D_2(a,r)] \right\}$$
$$- \int db \int_0^t ds\, \tilde{C}_g^{-1}(a,t-s/b) \int_0^s dr\, U(s-r)$$
$$\times \{[D_1(b,r) - D_2(b,r)]\}\,. \tag{43b}$$

As we know from Eq. (17) the result $\frac{dg(a,t)}{dt} = (\frac{dG(a,t)}{dt},\nu(\Gamma,0))$, we can write, by using Eq. (42), the result

$$\frac{dg(a,t)}{dt} = Z(a,t)g(a,t) - k\delta(a^* - a)g(a,t)$$
$$+ (F(a,t),\nu(\Gamma,0)) + (E(a,t),\nu(\Gamma,0)). \tag{44}$$

This is an exact equation for the probability distribution in a space, which is the reaction coordinate space. In the case of a nonreactive system ($k = 0$), the second and fourth terms on the right-hand side vanish identically and we get back the kinetic equation derived by Zwanzig [1] as well as by Garcìa-Colìn and Rio [3]. Equation (44) is a rather complicated equation at the outset and hence we use two consecutive approximations to transform it to a tractable form. For this purpose, we get back to Eq. (28), and we see that the first two terms eventually yield the random force. From the expression of the random force, it is again clear that it lies in the orthogonal space of $H_G(\omega/\Gamma)$. So for the extra term, it is quite physical to assume that it mainly belongs to $H_G(\omega/\Gamma)$. Here actually we are assuming that the portion of $G(a,t)$ that lies in the orthogonal space to $H_G(\omega/\Gamma)$ goes into the random force, and in the extra term, i.e., in $D_1(a,t) - D_2(a,t)$ wherever $G(a,t)$ appears, one can expand that in terms of orthogonal basis functions [7] [$G(b,0)$, where $b \in \mathbb{R}$], which span the Hilbert space $H_G(\omega/\Gamma)$. Hence one can write

$$G(a,t) = \int f(a,c,t)\, G(c,0)\, dc, \tag{45}$$

with $f(a,c,t)$ as the expansion coefficients, which can be obtained by multiplying Eq. (45) with $\omega(\Gamma)G(b,0)$, integrating over Γ, and then dividing both sides with $[G(b,0)]$. The final result is given by

$$f(a,b,t) = C(a,t/b). \tag{46}$$

By using Eq. (46) in Eq. (45), we obtain

$$G(a,t) = \int C(a,t/c)\, G(c,0)\, dc. \tag{47}$$

By substituting Eq. (47) into the expression of $D_1(a,t)$, we clearly see that $D_1(a,t) = D_2(a,t)$. Also from Eq. (43), we note that $[E(a,t),\nu(\Gamma,0)] = 0$. We also find that at the initial time, i.e., at $t = 0$, $G(a,t)$ belonged entirely to $H_G(\omega/\Gamma)$. So at least for small times, our approximation is very much justified. Again within the same approximation, as commonly used in the case of Brownian motion, we employ here the result $[F(a,t),\nu(\Gamma,0)] = 0$. Hence Eq. (44) takes the form

$$\frac{dg(a,t)}{dt} = Z(a,t)g(a,t) - k\delta(a^* - a)g(a,t). \tag{48}$$

Although the sink function has appeared in the argument of the exponential in the time-evolution equation of the phase-space function $A(\Gamma,t) = e^{i\tilde{L}^\dagger t}A(\Gamma,0)$ or the distribution function $\rho(\Gamma,t) = e^{-i\tilde{L}t}\rho(\Gamma,0)$, the speciality of Eq. (48) is that the Liouville operator that appears in the Zwanzig operator is the unmodified Liouville operator of the prereactive system (i.e., without the sink term). It is clear from Eq. (1) that in Liouville space, the diffusion of the phase-space coordinate Γ brings the system to the critical configuration that lies on the hypersurface $A(\Gamma) = a^*$, leading to the reaction. On the other hand, in a space, the diffusion of the phase-space function $A(\Gamma)$ is responsible for the attainment of the a^* configuration that results into the reaction. This shows clearly that the variable a or $A(\Gamma)$ represents the reaction coordinate, and the corresponding kinetic equation is given by Eq. (48).

It is, however, difficult to evaluate the memory kernel $K(a,a',s)$ owing to the appearance of the projection operator in $\exp{[-i\,(1-P_G)\,Ls]}$ in the full expression of the memory kernel $K(a,a',s)$. By assuming $(\partial A\,/\,\partial \mathrm{t})$ to be a slowly varying function, following Zwanzig [1], Eq. (48) can be simplified to obtain

$$\frac{\partial g(a,t)}{\partial t} + \sum_{j=1} \frac{\partial}{\partial a_j}[v_j(a)g(a,t)]$$
$$= \int_0^t ds \sum_{j=1}^{n}\sum_{k=1}^{n} \frac{\partial}{\partial a_j} W(a)K_{jk}\,(a;s)\,\frac{\partial}{\partial a_k}\frac{g\,(a,t-s)}{W(a)}$$
$$- k\delta(a-a^*)g\,(a,t) + O(\dot{A}^3 g), \tag{49}$$

where one has

$$K_{jk}\,(a;s) = [G(a,0)]^{-1}\,([\dot{A}_j(s) - v_j(a)]$$
$$\times [\dot{A}_k(0) - v_k(a)], G(a,0)),$$

$$\dot{A}_j(s) = \exp(isL)\dot{A}_j(0),$$
$$W(a) = [G(a,0)],$$
$$v_j(a) = \langle iLA_j(\Gamma,0); a\rangle = [G(a,0)]^{-1}(iLA_j(\Gamma,0), G(a,0)).$$

In the above expression, we write the set $a_1, a_2, \ldots, a_n$ as a in shorthand. Equation (49) has very nearly the structure of a Fokker-Planck equation with a sink term of strength k in a space. As illustrative examples, we now consider the application to ET and the diffusion-controlled reactions in the next two sections. In order to solve the kinetic equation [Eq.(49)], what is needed is the value of the sink position (a^*) as well as the expression for initial distribution function [$g(a,0)$] in a space, the evaluation of which is discussed below.

III. APPLICATION TO ET AND DIFFUSION-CONTROLLED REACTIONS

A. ET reaction

1. Identifying the phase-space function $A\,(\mathbf{\Gamma})$

While defining the phase-space function $A\,(\Gamma)$ in the present formalism, we first write the Hamiltonian for the reactant-product state of an ET reaction in a polar solvent in the general form

$$H^i(\Gamma) = H^i_{\text{sol}}(\Gamma) + H^i_{\text{el}} \quad (i = r,p), \tag{50}$$

where Γ denotes all the accessible geometrical coordinates of the solute and solvent molecules and the superscripts r and p correspond to the reactant and the product, respectively. Here H^i_{el} is the electronic term, independent of solvent motions, corresponding to the energy of the isolated reactant or product pair, and consists of two parts, viz., the Coulomb interaction between the net charges of the donor (z^i_d) and the acceptor (z^i_a) sites, separated by a distance R, and their electronic energies under vacuum. Here the quantity $H^i_{\text{sol}}(\Gamma)$ represents the solute-solvent and solvent-solvent interaction energy.

The electron, which is originally localized at the donor site in the reactant, will be delocalized when the following condition is satisfied [8–12], i.e.,

$$H^r_{\text{sol}}(\Gamma^*) - H^p_{\text{sol}}(\Gamma^*) = H^p_{\text{el}} - H^r_{\text{el}} \approx -\Delta G, \tag{51}$$

where Γ^* corresponds to the transition point in multidimensional configuration space, and ΔG represents the electronic energy contribution [9–12] of the solute particle to the free energy of the ET reaction in solution. In the case of a nonequilibrium situation, owing to the diffusion of the geometrical coordinates Γ in a downhill potential, the quantity $[H^r_{\text{sol}}(\Gamma) - H^p_{\text{sol}}(\Gamma)]$ acquires a specific value such as $-\Delta G$, whereas in the case of an equilibrium situation only the thermal fluctuations are responsible for bringing the same quantity to the desired value. Owing to thermal fluctuations, the only quantity that changes with the solvent configuration Γ and determines the ET is $[H^r_{\text{sol}}(\Gamma) - H^p_{\text{sol}}(\Gamma)]$, suggesting an obvious choice of the microscopic phase-space function $A(\Gamma)$ to be given by [9–12]

$$A(\Gamma) = \left[H^r_{\text{sol}}(\Gamma) - H^p_{\text{sol}}(\Gamma)\right]. \tag{52}$$

2. *Identifying the sink position a**

Now we consider the probability distribution for the reaction coordinate. The probability of the microscopic phase-space function $A(\Gamma)$ to have the value a, when the system is in the reactant-product state, is defined as

$$\exp\left[-\beta V^{\text{eff}}_i(a)\right] = \beta^{-1} \int d\Gamma \delta[A(\Gamma) - a] \exp\left[-\beta H^i_{\text{sol}}(\Gamma)\right], \tag{53}$$

where $W^i(a) = \exp[-\beta V^{\text{eff}}_i(a)]$ $(i = 1,2 \text{ for } r,p)$ corresponds to the projection of the respective distribution function for the reactant-product state in full phase space on the subspace described by the function $\delta[A(\Gamma) - a]$ directed along the one-dimensional coordinate a. An important advantage of defining such effective potential energy curves $V^{\text{eff}}_i(a)$ is that the solvent configurations [corresponding to those phase-space points that lie on the surface $A(\Gamma) = a$] along the reaction coordinate a are the same between the initial state (the electron is on the donor site) and the final state (the electron is on the acceptor site) because of the delta function. This property is very important because the position and orientations of the solvent molecules will be the same for all values of a, although the total energy is not always the same between the initial and final states. However, at the transition point a^*, the orientation and position of the solvent molecules are fixed and the energy conservation is also guaranteed when the following relation [10–12] holds, viz.,

$$\begin{aligned}
&\exp\left[-\beta V^{\text{eff}}_r(a^*)\right] \\
&\quad = \beta^{-1} \int d\Gamma \delta[A(\Gamma) - a^*] \\
&\qquad \times \exp\left\{-\beta H^p_{\text{sol}}(\Gamma) + \beta\left[H^p_{\text{sol}}(\Gamma) - H^r_{\text{sol}}(\Gamma)\right]\right\} \\
&\quad = \exp(\beta\Delta G)\beta^{-1} \int d\Gamma\, \delta[A(\Gamma) - a^*] \exp\left[-\beta H^p_{\text{sol}}(\Gamma)\right] \\
&\quad = \exp\left[-\beta V^{\text{eff}}_p(a^*) + \beta\Delta G\right].
\end{aligned} \tag{54}$$

The above derivation provides a relation between the effective potentials of the reactant and the product at the transition point a^*, viz.,

$$V^{\text{eff}}_r(a^*) = V^{\text{eff}}_p(a^*) - \Delta G. \tag{55}$$

Equation (55) actually provides a route for obtaining the transition point a^* for the occurrence of the ET reaction provided the explicit expression for $V^{\text{eff}}_i(a^*)$ is known. An alternative approach can also be used to derive a relation similar to the above equation, valid for all values of a, viz.,

$$\begin{aligned}
V^{\text{eff}}_r(a) &= -\beta^{-1} \ln\Bigg(\beta^{-1} \int d\Gamma\delta[A(\Gamma) - a] \\
&\qquad \times \exp\left\{-\beta H^p_{\text{sol}}(\Gamma) + \beta\left[H^p_{\text{sol}}(\Gamma) - H^r_{\text{sol}}(\Gamma)\right]\right\}\Bigg) \\
&= -\beta^{-1} \ln\Bigg\{\exp(-\beta a)\,\beta^{-1} \int d\Gamma\,\delta\,[A(\Gamma) - a] \\
&\qquad \times \exp\left[-\beta H^p_{\text{sol}}(\Gamma)\right]\Bigg\} \\
&= -\beta^{-1} \ln\left\{\exp\left[-\beta V^{\text{eff}}_p(a) - \beta a\right]\right\},
\end{aligned} \tag{56}$$

which can be rewritten as

$$V^{\text{eff}}_r(a) = V^{\text{eff}}_p(a) + a. \tag{57}$$

By combining Eq. (55) with Eq. (57), we obtain

$$a^* = -\Delta G. \tag{58}$$

The above relation is very important in the sense that the transition point is independent of the form of the effective potential $V^{\text{eff}}_i(a)$ but depends only on the free energy (ΔG) of the reaction.

3. *Initial distribution function [g(a,0)] in 'a' space*

We consider here a donor (D) and an acceptor (A) in a solvent environment. Prior to the absorption of a photon, the solvent molecules are in equilibrium with the D-A pair. Excitation of the DA pair with an ultrashort laser pulse leads to the formation of the ion pair D^+A^-. Thus, the ion pair is initially produced in a completely nonequilibrium configuration and then relaxes downward along the potential energy surface (corresponding to D^+A^-) through relaxation of the surrounding polar solvent until it meets the potential energy surface of the molecule *DA*, at which the configuration of the solvent molecules becomes the critical configuration, i.e., Γ^*, where the back ET takes place with an intrinsic rate constant k. In this situation, initially the phase-space coordinates Γ of the *D-A* solvent system are unknown owing to thermal fluctuations leading to new microscopic states for each repetition of the experiment with an identical macroscopic condition, i.e., $A(\Gamma,0) = (\hbar\omega - \Delta G) = a_0$, and instead what we know is only the probabilistic information about the initial Γ. Because prior to the excitation through the absorption of a photon, the system was in thermal equilibrium with a distribution function $\exp[-\beta H^r]$, the initial distribution corresponding to the excited state in Γ space is given by

$$\rho(\Gamma,0) = \frac{\delta\,[A(\Gamma,0) - (\hbar\omega - \Delta G)]\exp(-\beta H^r)}{\int d\Gamma\,\delta\,[A(\Gamma,0) - (\hbar\omega - \Delta G)]\exp(-\beta H^r)}. \tag{59}$$

Now, by combining Eqs. (6) and (59), we obtain the initial probability distribution $g(a,0)$ in a space as

$$\begin{aligned} g(a,0) &= \int d\Gamma\,\delta\,[A(\Gamma,0) - a] \\ &\quad\times \frac{\delta\,[A(\Gamma,0) - (\hbar\omega - \Delta G)]\exp(-\beta H^r)}{\int d\Gamma\,\delta\,[A(\Gamma,0) - (\hbar\omega - \Delta G)]\exp(-\beta H^r)} \\ &= \delta(a - (\hbar\omega - \Delta G)). \end{aligned} \tag{60}$$

This is an important result, because the effect of the excitation frequency ω has been introduced. In many situations, the *D-A* solvent system is initially in thermal equilibrium. In this situation, one has

$$g(a,0) = \int d\Gamma\,\delta\,[A(\Gamma) - a]\frac{\exp(-\beta H^r)}{\int d\Gamma\,\exp(-\beta H^r)}. \tag{61}$$

4. *Kinetic equation in one-dimensional ‘a’ space*

In this case, a is a scalar quantity and hence the coordinate a corresponds to one-dimensional space. Also, both $A(\Gamma,0)$ and $G(a,0)$ are symmetric under time reversal, whereas L is antisymmetric. Hence we clearly see that $v(a) = \langle iLA(t);a\rangle = 0$. In this situation, Eq. (49) simplifies to

$$\begin{aligned} \frac{\partial g(a,t)}{\partial t} &= \int_0^t ds\,\frac{\partial}{\partial a}W(a)K(a;s)\frac{\partial}{\partial a}\frac{g(a,t-s)}{W(a)} \\ &\quad - k\delta(a-a^*)g(a,t) + O(\dot{A}^3 g). \end{aligned} \tag{62}$$

Here $K(a;s)$ also can be written simply as $K(a;s) = \langle \dot{A}(s)\dot{A}(0);a\rangle$. It may be noted that several authors have previously written a similar type of equation phenomenologically and also applied it to the case of ET [13,14]. However, a rigorous derivation from first-principles theory is given here.

B. Diffusion-controlled reaction

1. *Initial distribution function* [$g(a,0)$] *in ‘a’ space*

Many authors have attempted to obtain a useful formulation for the description of chemical reactions influenced by diffusion effects. In this case, one has $A(\Gamma) = |\mathbf{r}_1 - \mathbf{r}_2| = r$, where $\mathbf{r}_1,\mathbf{r}_2$ represent the position vectors of the pair of reacting particles, and a^* is the contact distance. The initial distribution in a space is written as

$$g(a,0) = \int d\Gamma\delta(|\mathbf{r}_1 - \mathbf{r}_2| - a)\frac{\exp(-\beta H^r)}{\int d\Gamma\,\exp(-\beta H^r)}. \tag{63}$$

Now, we consider a pair of molecules within a volume V. The initial probability distribution for the two particles is given [15] by $p_{\text{eq}}(r) = g(r)/V$, where $g(r)$ represents the prereaction pair radial distribution function. Thus, the expression for $g(a,0)$ is further simplified as

$$g(a,0) = \frac{1}{V}\iint d\mathbf{r_1}\,d\mathbf{r_2}\delta(|\mathbf{r}_1 - \mathbf{r}_2| - a)g(r) = 2\pi a^2 g(a). \tag{64}$$

2. *Kinetic equation in one-dimensional ‘a’ space*

The kinetic equation for $g(a,t)$ can thus be written as

$$\begin{aligned} \frac{\partial g(a,t)}{\partial t} &= \int_0^t ds\,\frac{\partial}{\partial a}W(a)K(a;s)\frac{\partial}{\partial a}\frac{g(a,t-s)}{W(a)} \\ &\quad - k\delta(a-a^*)g(a,t) + O(\dot{A}^3 g), \end{aligned} \tag{65}$$

where the memory kernel $K(a;s)$ and effective potential $W(a)$ are defined, respectively, as

$$K(a;s) = \langle \dot{r}(s)\dot{r}(0);a\rangle, \tag{66}$$

$$W(a) = \ln\langle\delta(|\mathbf{r}_1 - \mathbf{r}_2| - a)\rangle = \ln\,g(a), \tag{67}$$

where $g(a)$ represents the pair distribution function in a space.

IV. CONCLUSION

In this work, we have derived an exact kinetic equation determining the time evolution of the probability distribution for general reaction coordinates starting from a modified Liouville equation, using the first-principle-based theory. By using two consecutive approximations along the lines of Zwanzig, we further simplify the kinetic equation to obtain a Fokker-Planck-type tractable equation with a sink term of strength k in reaction coordinate space (a space). As illustrative examples, we have considered applications to the ET and diffusion-controlled reactions. Here, we identify the reaction coordinates and the sink position, and we use appropriate initial conditions depending upon the experimental situation. In this case, we simplify the Fokker-Planck-type equation further by using time-reversal symmetry and the fact that the reaction coordinate is a scalar to obtain a non-Markovian Smoluchowski-type equation in one dimension. We have also shown that the effect of excitation frequency can be incorporated into the kinetic equation through the use of a suitable initial distribution function for solving the equation. A multidimensional Liouville space description is very cumbersome and highly involved, and hence a simpler description, such as the one-dimensional description presented here for these multidimensional processes, is very important and significant.

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