

Kinetics and Thermodynamics of Electron Transfer in Debye Solvents: An Analytical and Nonperturbative Reduced Density Matrix Theory

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A nonperturbative electron transfer rate theory is developed on the basis of reduced density matrix dynamics, which can be evaluated readily for the Debye solvent model without further approximation. Not only does it recover for reaction rates the celebrated Marcus' inversion and Kramers' turnover behaviors, but the present theory also predicts reaction thermodynamics, such as equilibrium Gibbs free energy and entropy, some interesting solvent-dependent features that are calling for experimental verification. Moreover, a continued fraction Green's function formalism is also constructed, which can be used together with the Dyson equation technique for efficient evaluation of nonperturbative reduced density matrix dynamics.

I. Introduction

Solvent environment plays a crucial role in determining chemical kinetic properties. Its interaction induces fluctuation that compensates for the activation energy and also results in relaxation that stabilizes the reaction product. This dual role of solvent interaction, related via fluctuation–dissipation relation, has been recognized since Einstein in his study of Brownian motion.¹ The effect of solvent interaction on chemical kinetics was first studied by Kramers in his classical Fokker–Planck equation (FPE) approach to the rate theory of isomerization reaction.² This is a classical reduced equation-of-motion (EOM) approach, in which the chemical reaction is treated as an escape over the barrier of particles moving in a one-dimensional potential surface and is subject to a Langevin force originated from the stochastic solvent interaction. The resulting rate, as a function of solvent viscosity, exhibits a turnover behavior: It increases linearly with viscosity initially, reaches a maximum at an intermediate viscosity value, and falls off inversely as viscosity in the high-friction regime.^{2,3}

Electron-transfer (ET) processes constitute another class of systems whose dependence on solvent environment has been extensively studied since Marcus' pioneering contribution.^{4–6}

Consider the simplest ET system in which the total Hamiltonian reads

$$H_T = h_a|a\rangle\langle a| + (h_b + E^\circ)|b\rangle\langle b| + V(|a\rangle\langle b| + |b\rangle\langle a|) \quad (1)$$

Here, h_a and h_b are the solvent Hamiltonians for the ET system in the donor and acceptor states, respectively, E° is the reaction endothermicity, and V is the transfer coupling matrix element. The system is initially in the donor $|a\rangle$ site, with the solvent (bath) equilibrium density matrix $\rho_a^{\text{eq}} \propto e^{-h_a/(k_B T)}$ at the temperature T . The reaction coordinate is now $U \equiv h_b - h_a$, which

is purely of solvent nature and called the solvation coordinate. Its static mean, $\lambda = \langle U \rangle \equiv \text{tr}(U\rho_a^{\text{eq}})$, denotes the solvent reorganization energy, while its variation satisfies $\langle U^2 \rangle - \langle U \rangle^2 \approx 2\lambda k_B T$, the classical fluctuation–dissipation relation in the high-temperature limit. With a classical dielectric continuum model, Marcus had further related the solvent reorganization energy λ to the static and high-frequency dielectric constants (ϵ_0 and ϵ_∞) of the solvent.^{4–6}

The standard approach to ET rates is based on correlation function formalism.^{4–19} The second-order transfer correlation function is related to the nonadiabatic rate theory,^{7–9} which in the static solvation limit assumes the celebrated Marcus' rate expression^{4–6}

$$k = \frac{V^2/\hbar}{\sqrt{\lambda k_B T/\pi}} \exp\left[-\frac{(E^\circ + \lambda)^2}{4\lambda k_B T}\right] \quad (2)$$

Rates have also been formulated on the basis of fourth-order transfer correlation functions, followed by certain resummation schemes that partially account for the effect of nonperturbative transfer coupling.^{7,10–19} The resulting rates do recover the celebrated Kramers' turnover behavior^{2,3} and are also able to relate the reaction adiabaticity to the solvent relaxation time scale. However, these correlation function-based rate theories remain perturbative in nature. To obtain rate expressions, one shall also assume the separation of time scales between the fast ET dynamics and the slow solvation processes.^{7,10–19} As a result, the reaction Gibbs free energy ΔG° , obtained via ratio of the forward and backward rates $k/k' = \exp[-\Delta G^\circ/(k_B T)]$, is identical to the endothermicity parameter E° that contains no explicit dependence on solvent environment. The parabolic dependence of $\log k$ on E° , as shown by eq 2, can be read as its dependence on ΔG° . This is the so-called Marcus' inversion behavior.^{4–6}

An alternative approach to ET rates is via reduced density matrix,^{20,21} defined formally as $\rho(t) \equiv \text{tr}_B \rho_T(t)$, the trace of total density matrix over bath degrees of freedom. This is a quantum

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reduced EOM approach in which the transfer coupling is part of the system and can be treated exactly. However, the system–bath interaction, which in ET systems is neither weak nor Markovian, constitutes the major challenge in the general theory of quantum dissipation.^{22–24}

It has been shown that an exact reduced dynamics theory, in terms of hierarchically coupled EOM, does exist in model Debye solvents that satisfies a semiclassical fluctuation–dissipation relation.^{24,25} On the basis of this exact theory, we shall in this work construct an analytical rate expression for the simple ET system, without invoking resummation and time scale separation approximations. As a result, the present work will not just recover for kinetic rates the celebrated Kramers' turnover^{2,3} and Marcus' inversion^{4–6} behaviors, but it will also reveal for ET thermodynamics such as Gibbs free energy and entropy functions some interesting solvent-dependent behaviors.

The remainder of this paper is organized as follows. Section II treats an exact, nonperturbative theory of the reduced density matrix dynamics in Debye solvents. After a brief review of the hierarchical EOM formalism (section II.A),^{24,25} we construct a continued fraction Green's function theory of quantum dissipation (section II.B). We further utilize it, together with Dyson equation technique, to evaluate analytically the reduced dynamics of the simple ET system (section II.C). Section III contributes to the development of reduced density matrix based ET rate theory. Numerical studies in section IV will demonstrate not just for ET rates, but also for ET reaction equilibrium thermodynamics, their dependence on the solvent environment. Finally, section V concludes the paper.

II. Exact Reduced Dynamics in Debye Solvents

A. Hierarchical Equations of Motion Formalism. To describe the hierarchical EOM for the reduced density matrix,^{24,25} let us recast the total ET Hamiltonian (eq 1) in the stochastic bath interaction picture

$$H_T(t) = H + H'(t) \quad (3)$$

with H and $H'(t)$ representing the reduced system Hamiltonian and the stochastic system–bath coupling, respectively.

$$H = (E^\circ + \lambda)|b\rangle\langle b| + V(|a\rangle\langle b| + |b\rangle\langle a|) \quad (4)$$

$$H'(t) = [U(t) - \lambda]|b\rangle\langle b| \quad (5)$$

The stochastic solvation coordinate

$$U(t) \equiv e^{ih_a t/\hbar} U e^{-ih_a t/\hbar} \equiv e^{ih_a t/\hbar} (h_b - h_a) e^{-ih_a t/\hbar} \quad (6)$$

is assumed to be of Gaussian statistics. Thus, the effects of solvent on the ET system are completely determined by the solvent reorganization energy

$$\lambda = \langle U(t) \rangle \equiv \text{tr}[U(t)\rho_a^{\text{eq}}] = \langle U \rangle \quad (7)$$

and the solvation correlation function

$$C(t - \tau) = \langle [U(t) - \lambda][U(\tau) - \lambda] \rangle \quad (8)$$

In this work, we focus on the ET system in a Debye solvent (also called the Drude model), characterized by the following form of solvation response function²²

$$i\langle [U(t), U(0)] \rangle = -2 \text{Im } C(t) = 2\Theta(t)\hbar\lambda\gamma e^{-\gamma t} \quad (9)$$

Here, $\Theta(t)$ is the Heaviside step function and $\gamma^{-1} \equiv \tau_L =$

$\tau_D(\epsilon_\infty/\epsilon_0)$, with τ_D being the Debye time parameter and ϵ_0 (ϵ_∞) the static (high-frequency) dielectric constant of the solvent. The corresponding solvation correlation function in the semiclassical high-temperature limit reads²²

$$C(t) \approx \lambda(2k_B T - \hbar\gamma) e^{-\gamma t} \quad (10)$$

For this model, the exact reduced density matrix dynamics has been constructed in terms of^{24,25}

$$\dot{\rho}_n = -(i\mathcal{L} + n\gamma)\rho_n - i\mathcal{B}\rho_{n+1} - in\mathcal{A}\rho_{n-1}; \quad n \geq 0 \quad (11)$$

which hierarchically couple the $\rho \equiv \rho_0$ of primary interest and a set of auxiliary system operators $\{\rho_n; n = 1, 2, \dots\}$. The initial conditions are $\rho_n(0) = \rho(0)\delta_{n0}$ and

$$\hat{\mathcal{O}} \equiv \hbar^{-1}[H, \hat{O}] \quad (12a)$$

$$\mathcal{A}\hat{O} \equiv \frac{2\lambda k_B T}{\hbar^2} [|b\rangle\langle b|, \hat{O}] - i\frac{\lambda\gamma}{\hbar} \{|b\rangle\langle b|, \hat{O}\} \quad (12b)$$

$$\mathcal{B}\hat{O} \equiv [|b\rangle\langle b|, \hat{O}] \quad (12c)$$

Here, $\{\cdot, \cdot\}$ denotes anticommutator. It has been shown²⁴ that the individual auxiliary operator $\rho_{n>0}$ accounts for the $(2n)$ th-order system–bath interaction contribution to the reduced dynamics of the primarily interested ρ ; see also the comments in the last paragraph of section II.B.

B. Continued Fraction Green's Function Formalism.

Introduce the propagators $\{\mathcal{U}_n(t); n = 0, 1, \dots\}$:

$$\rho_n(t) \equiv e^{-n\gamma t} \mathcal{U}_n(t) \rho(0) \quad \text{with } \mathcal{U}_n(0) = \delta_{n0} \quad (13)$$

Equation 11 reads now

$$\dot{\mathcal{U}}_n(t) = -i\mathcal{L}\mathcal{U}_n(t) - i\mathcal{B}e^{-\gamma t}\mathcal{U}_{n+1}(t) - in\mathcal{A}e^{\gamma t}\mathcal{U}_{n-1}(t)$$

which in the Laplace domain is

$$(s + i\mathcal{L})\tilde{\mathcal{U}}_n(s) + i\mathcal{B}\tilde{\mathcal{U}}_{n+1}(s + \gamma) + in\mathcal{A}\tilde{\mathcal{U}}_{n-1}(s - \gamma) = \delta_{n0} \quad (14)$$

Define the Green's functions $\{\mathcal{G}^{(n)}(s); n \geq 0\}$ via

$$\tilde{\mathcal{U}}_0(s) \equiv \mathcal{G}^{(0)}(s) \equiv \mathcal{G}(s) \quad (15a)$$

$$\tilde{\mathcal{U}}_n(s) \equiv -in\mathcal{G}^{(n)}(s)\mathcal{A}\tilde{\mathcal{U}}_{n-1}(s - \gamma); \quad n > 0 \quad (15b)$$

These equations will lead to

$$\mathcal{G}^{(n)}(s) = \frac{1}{s + i\mathcal{L} + \Pi^{(n)}(s)}; \quad n \geq 0 \quad (16a)$$

with

$$\Pi^{(n)}(s) \equiv (n + 1)\mathcal{B}\mathcal{G}^{(n+1)}(s + \gamma)\mathcal{A} \quad (16b)$$

The above equations, which can be recast as

$$\Pi^{(n)}(s) = \mathcal{B} \frac{n + 1}{s + \gamma + i\mathcal{L} + \Pi^{(n+1)}(s + \gamma)} \mathcal{A} \quad (17)$$

constitute the infinite continued fraction formalism for evaluating each individual $\Pi^{(n)}(s)$ or $\mathcal{G}^{(n)}(s)$.

The Green's function $\mathcal{G}^{(0)} \equiv \mathcal{G}$ and its associated $\Pi^{(0)} \equiv \Pi$ are of the primary interest. The former resolves the reduced

density matrix evolution (cf. eq 15a and eq 13 with $n = 0$)

$$\tilde{\rho}(s) \equiv \int_0^\infty dt e^{-st} \rho(t) = \mathcal{G}(s) \rho(0) \quad (18)$$

This equation can be rewritten as (cf. eq 16a at $n = 0$)

$$s\tilde{\rho}(s) - \rho(0) = -i\mathcal{L}\tilde{\rho}(s) - \Pi(s)\tilde{\rho}(s) \quad (19)$$

which in the time domain reads

$$\dot{\rho}(t) = -i\mathcal{L}\rho(t) - \int_0^t d\tau \hat{\Pi}(t - \tau) \rho(\tau) \quad (20)$$

Therefore

$$\Pi(s) = \Pi^{(0)}(s) = \int_0^\infty dt e^{-st} \hat{\Pi}(t) \quad (21)$$

represents the memory kernel in the Laplace domain.

The initial input for the inverse recursive evaluation of $\Pi(s)$ (eq 17) can be chosen on the basis of the following observation. Each \mathcal{A} is of second order in the system–bath coupling; thus, the leading contribution of $\Pi^{(n)}$ to the required Π is of the $(2n+2)$ th order. Moreover, as the mathematical nature of the continued fraction, convergency is also guaranteed practically for arbitrary strength and time scale of system–bath coupling. We can therefore set $\Pi^{(N+1)} = 0$, with a sufficiently large N , to initiate the inverse recursive procedure, and evaluate $\Pi^{(n)}(s + n\gamma)$, first at $n = N$, then $N - 1$, and so on, until the required $\Pi^{(0)}(s) = \Pi(s)$ is reached.

C. Evaluation of Tensor Elements. The tensor element of a superoperator (or Liouville-space operator) \mathcal{O} is defined in the double-bracket notation as^{26,27}

$$\mathcal{O}_{jj',kk'} \equiv \langle\langle jj' | \mathcal{O} | kk' \rangle\rangle \quad (22)$$

so that

$$\mathcal{O} = \sum_{jj',kk'} \mathcal{O}_{jj',kk'} |jj'\rangle\langle\langle kk'| \quad (23)$$

For a two-level system considered in this work, each tensor has $2^4 = 16$ elements. That \mathcal{O} is Hermite implies $\mathcal{O}_{jj',kk'}^* = \mathcal{O}_{jj',kk'}^*$. Apparently, all $\Pi^{(n)}$ and $\mathcal{G}^{(n)}$ are Hermite.

To analyze the tensor elements of $\Pi^{(n)}$ (eq 16b), let us first examine \mathcal{A} and \mathcal{B} , defined by eqs 12b and 12c, respectively. They are found to be diagonal, with the nonzero elements of $\mathcal{A}_{ba,ba} = -\mathcal{A}_{ab,ab}^* = \lambda(2k_B T - i\hbar\gamma)/\hbar^2$, $\mathcal{A}_{bb,bb} = -i2\lambda\gamma/\hbar$, and $\mathcal{B}_{ba,ba} = -\mathcal{B}_{ab,ab}^* = 1$. As a result, the only nonzero elements in $\Pi^{(n)}$ (eq 16b) are

$$x^{(n)} \equiv \Pi_{ba,ba}^{(n)}, \quad y^{(n)} \equiv \Pi_{ba,ab}^{(n)}, \quad z^{(n)} \equiv \Pi_{ba,bb}^{(n)} \quad (24)$$

and their Hermitian conjugate elements, and they are related to the Green's function tensor elements

$$X^{(n)} \equiv \mathcal{G}_{ba,ba}^{(n)}, \quad Y^{(n)} \equiv \mathcal{G}_{ba,ab}^{(n)}, \quad Z^{(n)} \equiv \mathcal{G}_{ba,bb}^{(n)} \quad (25)$$

by [denoting $\eta \equiv \lambda(2k_B T - i\hbar\gamma)/\hbar^2$]

$$x^{(n)}(s) = \eta(n+1) X^{(n+1)}(s + \gamma) \quad (26a)$$

$$y^{(n)}(s) = -\eta^*(n+1) Y^{(n+1)}(s + \gamma) \quad (26b)$$

$$z^{(n)}(s) = (\eta - \eta^*)(n+1) Z^{(n+1)}(s + \gamma) \quad (26c)$$

To evaluate the involving Green's function elements via eq 16a, we apply the Dyson equation

$$\mathcal{G} = \bar{\mathcal{G}} - \bar{\mathcal{G}}(i\mathcal{L}' + \Pi')\mathcal{G} \quad (27)$$

with $\bar{\mathcal{G}}$ being the diagonal contribution and \mathcal{L}' and Π' the off-diagonal parts of the involving \mathcal{L} and Π in eq 16a, respectively. Here and in eqs 28 and 29 that follow, the common superscript (n) and argument s in both sides of equations are implied. After some elementary algebra, we obtain

$$X = \frac{\alpha^* + \beta^*}{|\alpha + \beta|^2 - |\beta - y|^2} \quad (28a)$$

$$Y = \frac{\beta - y}{|\alpha + \beta|^2 - |\beta - y|^2} \quad (28b)$$

$$Z = -\frac{1}{s} [(z - iV/\hbar)X + (z^* + iV/\hbar)Y] \quad (28c)$$

with

$$\alpha \equiv s + (i/\hbar)(E^o + \lambda) + x \quad (29a)$$

$$\beta \equiv s^{-1}(V/\hbar)^2(2 + i\hbar z/V) \quad (29b)$$

We have thus established from eq 16a the expressions of $\{X, Y, Z\}^{(n)}(s)$ in terms of $\{x, y, z\}^{(n)}(s)$, which together with eq 26 constitute an analytical and exact formalism for the inverse recursive evaluation of the reduced dynamics in Debye solvents. In the following section, we shall show that the ET reaction rate can be expressed in terms of $\{x, y, z\}$, i.e., the nonzero elements of dissipative memory kernel Π in the Laplace domain.

III. Electron-Transfer Rate: Reduced Density Matrix Formalism

We are now in the position to construct the reduced density matrix approach to ET rates. Let us start with $\tilde{\rho}(s)$ (eq 19), where $\rho(t=0) = |aa\rangle\rangle$. By separating $\tilde{\rho}(s)$ into population vector $\tilde{\mathbf{P}} = [\tilde{\rho}_{aa}, \tilde{\rho}_{bb}]^T$ and coherent vector $[\tilde{\rho}_{ab}, \tilde{\rho}_{ba}]^T$ components, and then using eq 19 to eliminate the latter, we obtain the ET kinetic equations in Laplace domain as

$$s\tilde{\mathbf{P}}(s) - \mathbf{P}(0) = K(s)\tilde{\mathbf{P}}(s) \quad (30)$$

with

$$K(s) = T_{PC}(s + T_{CC})^{-1} T_{CP} - T_{PP} \quad (31)$$

Here, T_{PC} , T_{CC} , T_{CP} , and T_{PP} denote the coherence-to-population, coherence-to-coherence, population-to-coherence, and population-to-population transfer matrices involved in $(i\mathcal{L}' + \Pi)$, respectively; cf. eq 19. Tensor analysis (cf. section II.C) results in $T_{PP} = 0$ and

$$T_{PC} = \frac{iV}{\hbar} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}, \quad T_{CP} = T_{PC} + \begin{bmatrix} 0 & \Pi_{ba,bb}^* \\ 0 & \Pi_{ba,bb} \end{bmatrix} \quad (32a)$$

$$T_{CC} = \frac{i}{\hbar}(E^\circ + \lambda) \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} \Pi_{ba,ba}^* & \Pi_{ba,ab}^* \\ \Pi_{ba,ab} & \Pi_{ba,ba} \end{bmatrix} \quad (32b)$$

Note that eq 30 in time domain reads

$$\dot{\mathbf{P}}(t) = \int_0^t d\tau \hat{K}(t - \tau) \mathbf{P}(\tau) \quad (33)$$

Thus, $K(s)$ is the resolution or the Laplace transform of the memory rate kernel $\hat{K}(t)$. The total population conservation implies the relation $K_{aj} + K_{bj} = 0$; thus, eq 33 is equivalent to

$$\dot{P}_a(t) = - \int_0^t d\tau \hat{k}(t - \tau) P_a(\tau) + \int_0^t d\tau \hat{k}'(t - \tau) P_b(\tau) \quad (34)$$

The forward and backward rate resolutions are

$$k(s) = -K_{aa}(s) = \int_0^\infty dt e^{-st} \hat{k}(t) \quad (35a)$$

$$k'(s) = K_{ab}(s) = \int_0^\infty dt e^{-st} \hat{k}'(t) \quad (35b)$$

Together with eqs 31–32 and $T_{pp} = 0$, we obtain

$$k(s) = \frac{2|V|^2}{\hbar^2} \text{Re} \frac{\alpha(s) + y(s)}{|\alpha(s)|^2 - |y(s)|^2} \quad (36a)$$

and

$$k'(s) = \frac{2|V|^2}{\hbar^2} \text{Re} \frac{[\alpha(s) + y(s)][1 - i\hbar z^*(s)/V]}{|\alpha(s)|^2 - |y(s)|^2} \quad (36b)$$

Here, $\alpha(s) = s + (i/\hbar)(E^\circ + \lambda) + x(s)$ is the same as eq 29a, while $x \equiv \Pi_{ba,ba} \equiv x^{(0)}$, $y \equiv \Pi_{ba,ab} \equiv y^{(0)}$, and $z \equiv \Pi_{ba,bb} \equiv z^{(0)}$ are the same as eq 24 at $n = 0$.

The above formulations relate the ET reaction rate resolutions $k(s)$ and $k'(s)$ to the memory dissipation kernel resolution $\Pi(s)$; cf. eqs 19 and 20. The analytical expressions for the inverse recursive evaluation of the $\Pi(s)$ tensor elements had been detailed in sections II.B.C. We have thus completed the analytical expressions for the frequency-dependent rates of ET in Debye solvents.

IV. Rates versus Thermodynamics: Numerical Demonstrations

For numerical study, we focus on the ET rate constants, $k \equiv k(s = 0)$ and $k' \equiv k'(s = 0)$, which amount to the integrated memory rate kernel (cf. eq 35). It is easy to show that in the weak transfer coupling (small V) and slow solvation (small γ) limit, the present rate constant k (eq 36a at $s = 0$) recovers the celebrated Marcus' ET rate expression of eq 2. We shall also be interested in the reaction Gibbs free energy, $\Delta G^\circ = -k_B T \ln(k/k')$, entropy $\Delta S^\circ = -\partial \Delta G^\circ / \partial T$, and enthalpy $\Delta H^\circ = \Delta G^\circ + T \Delta S^\circ$. We shall demonstrate how the rate constants and reaction thermodynamics functions depend on the model parameters, reaction endothermicity E° , solvent reorganization energy λ , and longitudinal relaxation time $\tau_L = 1/\gamma$. The other two parameters of the model are set to be $T = 298$ K and $V = 1$ kJ/mol, unless further specified. In fact, the value of V can be considered as the unit that scales other parameters used. The temperature should also vary around $T = 298$ K in order to numerically evaluate entropy.

Note that, in optical spectroscopy, one often uses a dimensionless parameter, $\kappa^{-1} = \tau_L \sqrt{2k_B T \lambda} / \hbar$, to measure the slow ($\kappa \ll 1$) and fast ($\kappa \gg 1$) solvent modulation limits. For $\lambda = 3$ kJ/mol at $T = 298$ K, $\kappa = 1$ corresponds to $\tau_L = 16.5$ fs, while

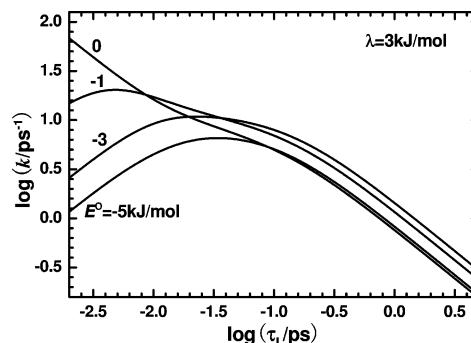


Figure 1. Electron-transfer rates as the functions of solvent longitudinal relaxation time $\tau_L \equiv 1/\gamma$, for some specified values of endothermicity E° . The solvent reorganization energy, transfer coupling strength, and temperature are $\lambda = 3$ kJ/mol, $V = 1$ kJ/mol, and $T = 298$ K, respectively.

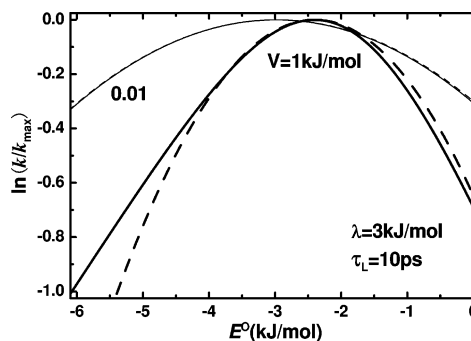


Figure 2. The normalized rates, in the slow modulation regime ($\tau_L = 10$ ps), as the functions of E° . The Marcus' parabolic relation, $\ln(k/k_{\max}) = -(E^\circ + \lambda)^2 / (4k_B T \lambda)$, where $\lambda = 3$ kJ/mol, is recovered in the case of $V = 0.01$ kJ/mol, but not for $V = 1$ kJ/mol. The latter case does not fit well with a parabolic function (dash curve); see the text for details.

the typical ET solvation correlation time scale is picoseconds. We will show that the parameter κ can also be used in the ET rate problem.

Figure 1 depicts ET rate k as the function of solvent relaxation time $\tau_L = 1/\gamma$ at four representative values of endothermicity, $E^\circ = 0, -1, -3$, and -5 kJ/mol. The solvent reorganization energy $\lambda = 3$ kJ/mol.

In general, the ET rate consists of the barrier crossing and the coherent tunneling contributions. When $E^\circ = 0$ (symmetric case), the system is in Fermi resonance, and the ET is dominated by coherent tunneling. The observed rate in this case exhibits the motional narrowing behaviors.^{7,28} The faster the solvent modulation is, the larger the coherent resonant tunneling rate will be. In a nonsymmetric ($E^\circ \neq 0$) system, the barrier crossing is significant, and the observed ET rate exhibits clearly the Kramers' turnover behaviors.^{2,3}

The rates observed in the slow solvent modulation (large τ_L , which amounts to large viscosity) region of Figure 1 are closely related to the Marcus' inversion behaviors. Figure 2 depicts the ET rate, in terms of $\ln(k/k_{\max})$, as the function of reaction endothermicity E° , in the slow modulation region ($\tau_L = 10$ ps), at two specified values of transfer coupling strength, $V = 0.01$ and 1 kJ/mol. When the transfer coupling is small ($V = 0.01$ kJ/mol), the rate in the slow solvent modulation regime does have the Marcus' nonadiabatic form, $\ln(k/k_{\max}) = -(E^\circ + \lambda)^2 / (4k_B T \lambda)$ of eq 2; cf. the thin-solid vs thin-dash curves. In the case of $V = 1$ kJ/mol, however, the rate deviates significantly

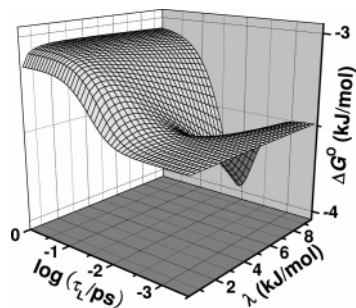


Figure 3. Reaction Gibbs free energy ΔG° as the function of solvent parameters (λ , τ_L), for an ET system with $E^\circ = -3$ kJ/mol and $V = 1$ kJ/mol at $T = 298$ K.

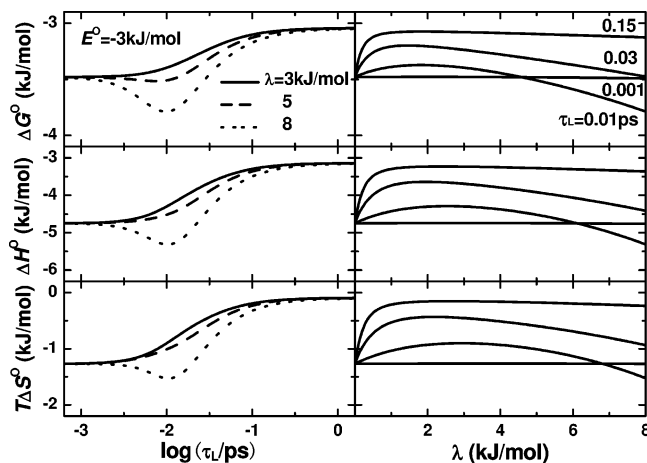


Figure 4. Reaction thermodynamics functions ΔG° , ΔS° , and ΔH° : (left) as the functions of τ_L at some selected values of λ ; (right) as the functions of λ at some selected values of τ_L . The ET system is the same as that of Figure 3.

from the Marcus' expression. The poorly fitted parabolic function there, $-(E^\circ - E_{\max}^\circ)^2/(\zeta 4k_B T \lambda)$ (dash-curve), is found to be $E_{\max}^\circ = -2.4$ kJ/mol and $\zeta = 0.3$.

Figure 3 shows the 3D plot of reaction Gibbs free energy ΔG° as a function of (λ , τ_L), exemplified at $T = 298$ K with $E^\circ = -3$ kJ/mol and $V = 1$ kJ/mol. Reported in Figure 4 are some representing 2D slices of Figure 3 for ΔG° , together with the numerically evaluated reaction entropy ΔS° and enthalpy ΔH° . The observed features here are listed as follows:

(i) The basic symmetry requirements, such as $\Delta G^\circ(-E^\circ) = -\Delta G^\circ(E^\circ)$, which implies also $\Delta G^\circ(E^\circ = 0) = 0$, hold in general.

(ii) ΔG° , ΔH° , and E° are of the same sign and $|\Delta H^\circ| \geq |\Delta G^\circ| \geq |E^\circ|$, implying that the enthalpy and the entropy play opposite roles on the reaction Gibbs free energy.

(iii) The dependence of ΔG° on (λ , τ_L), as shown in Figure 3, is qualitatively similar to that in the weak transfer coupling regime.

(iv) In general, ΔG° approaches a constant in both the fast ($\kappa \gg 1$) and slow ($\kappa \ll 1$) modulation regimes. The smaller V is, the closer ΔG° to E° will be. For the system demonstrated in Figure 3 (or Figure 4) where $E^\circ = -3$ kJ/mol with $V = 1$ kJ/mol, $|\Delta G^\circ(\kappa \gg 1)| > |\Delta G^\circ(\kappa \ll 1)|$; however, the sign could be opposite for small $|E^\circ|$ systems (not shown here).

(v) In the modest modulation regime ($\kappa \approx 1$), the reaction thermodynamic functions (ΔG° , ΔH° , and ΔS°) exhibit certain nonlinear dependence on (λ , τ_L). In particular, the magnitudes of these ET reaction thermodynamic functions are of maximum values around $\kappa \approx 1$ when $\lambda > |E^\circ|$.

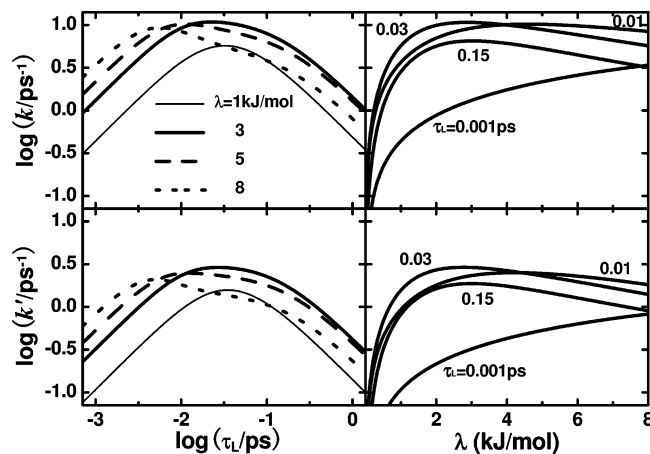


Figure 5. The forward and backward rate constants, k (upper panels) and k' (lower panels), relevant to the reaction thermodynamics functions in Figure 4.

Interestingly, the observed Kramers' turnover of rates occurs also around the $\kappa \approx 1$ (intermediate friction) region. The relevant forward and backward rate constants are given in Figure 5. This may at least partially account for the non-monotonic dependence of thermodynamics functions on the solvent environment in this region, as they are related to the rates via the detailed balance relation.

V. Summary

In summary, we have constructed a formally exact, nonperturbative ET rate theory in terms of the resolution of the memory dissipation kernel (cf. eq 36 with eqs 21 and 24). For Debye solvents in which the solvation correlation is characterized by an exponential function (eq 10), the ET rates, or rate resolutions in general (eq 36), can be evaluated readily via the inverse-recursion formalism (cf. eq 26 with eq 28). Not only does it recover the celebrated Marcus' inversion and Kramers' turnover behaviors of the ET rates, the present formalism also provides a microscopic theory for the effects of solvent environment on the ET thermodynamics. The dependence of reaction thermodynamics on solvent environment is found to be quite dramatic, especially in the region where the Kramers turnover occurs. This observation suggests the possibility of utilizing the thermodynamics data to extract such as the solvation correlation time parameter (cf. the left panel of Figure 4).

This work has also developed a nonperturbative theory of reduced density matrix dynamics, in terms of continued fraction Green's function (section II.B). This formalism can be used together with the Dyson equation technique for efficient and analytical evaluation of reduced dynamics (section II.C). The present formalism is exact for the Debye solvents (eq 10). However, as the semiclassical fluctuation-dissipation theorem is involved in eq 10, the reduced density matrix and rates may become negative if $k_B T \ll (|V|^2 + 1/4|E^\circ|^2)^{1/2}$. Generalization of the present continued fraction Green's function approach to non-Debye solvents at arbitrary temperature is feasible and will be developed in the future.

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