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 based on the 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, the present theory also predicts for 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 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 chemical reaction is treated as escape over barrier of particle moving in one-dimensional potential surface and subject to a Langevin force originated from stochastic solvent interaction. The resulting rate, as function of solvent viscosity, exhibits a turnover behavior: it increases linearly as viscosity initially, reaches a maximum at an intermediate viscosity value, and falls off inversely as viscosity in the high friction regime.3

Electron transfer (ET) processes constitute another class of systems whose dependence on solvent environment has been extensively studied since Marcus’ pioneering contribution.4,5,6 Consider the simplest ET system in which the total Hamiltonian reads

\[ H_T = h_a|a\rangle\langle a| + (h_b + E^\circ)|b\rangle\langle b| + V(|a\rangle\langle b| + |b\rangle\langle a|). \]  (1)

Here, \( h_a \) and \( h_b \) are the solvent Hamiltonians for the ET system in the donor and acceptor states, respectively, \( E^\circ \) is the reaction endothermicity, and \( V \) the transfer coupling matrix element. The system is initially in the donor \( |a\rangle \) site, with the solvent (bath) equilibrium density matrix \( \rho_n^\text{eq} \propto e^{-h_a/(k_BT)} \) at the temperature \( T \). The reaction coordinate is now \( U = h_b - h_a \), which is purely of solvent in nature and called the solvation coordinate. Its static mean, \( \lambda = \langle U \rangle \equiv \text{tr}(U\rho_n^\text{eq})/\text{tr}(\rho_n^\text{eq}) \), denotes the solvent reorganization energy, while its variation satisfies \( \langle U^2 \rangle - \langle U \rangle^2 \approx 2\lambda k_BT \), the classical fluctuation-dissipation relation in the high temperature limit. With a classical dielectric continuum model, Marcus had further related the solvent reorganization energy \( \lambda \) to the static and high-frequency dielectric constants of the solvent.4,5,6

The standard approach to ET rates is based on correlation function formalism4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21 The second-order transfer correlation function is related to the nonadiabatic rate theory7,8,9 which in the static solvation limit assumes the celebrated Marcus’ rate expression4,5,6

\[ k = \frac{V^2/h}{\sqrt{\lambda k_BT/\pi}} \exp\left[-\frac{(E^\circ + \lambda)^2}{4\lambda k_BT}\right]. \]  (2)

Rates have also been formulated based on fourth-order transfer correlation functions, followed by certain resummation schemes that partially account for the effect of nonperturbative transfer coupling7,10,11,12,13,14,15,16,17,18,19,20,21 The resulting rates do recover the celebrated Kramers’ turnover behavior2,3 and are also able to relate the reaction adiabaticity to 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 processes7,10,11,12,13,14,15,16,17,18,19,20,21 As results, the reaction Gibbs free-energy \( \Delta G^\circ \), obtained via the forward and backward rates ratio \( k/k' = \exp[-\Delta G^\circ/(k_BT)] \), is identical to the endothermicity parameter \( E^\circ \) that contains no explicit dependence on solvent environment. The parabolic dependence of \( \log k \) on \( E^\circ \), as shown by eq (2), can be read as its dependence on \( \Delta G^\circ \). This is the so-called Marcus’ inversion behavior4,5,6

Alternative approach to ET rates is via reduced density matrix formalism20,21 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 reduced EOM approach in which the trans-
fer 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.

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. Based on this exact theory, we shall in this work construct an analytical rate expression for the simple ET system, without invoking such as resummation and timescale separation approximations. As results, the present work will not just recover for kinetic rates the celebrated Kramers’ turnover and Marcus’ inversion behaviors, 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 (Sec. II A),24,25 we construct a continued fraction Green’s function theory of quantum dissipation (Sec. II B). We further utilize it, together with Dyson equation technique, to evaluate analytically the reduced dynamics of the simple ET system (Sec. II C). Section III contributes to the development of reduced density matrix-based ET rate theory. Numerical studies in Sec. IV will demonstrate not just for ET rates, but also for ET reaction (equilibrium) thermodynamics, their dependence on solvent environment. Finally, Sec. V concludes the paper.

II. EXACT REDUCED DYNAMICS IN DEBYE SOLVENTS

A. Hierarchical equations of motion formalism

To describe the hierarchical EOM for reduced density matrix24,25 let us recast the total ET Hamiltonian (eq 1) in the stochastic bath interaction picture,

\[ H_T(t) = H + H'(t), \]

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

\[ H = (E^a + \lambda)|b\rangle\langle b| + V(|a\rangle\langle b| + |b\rangle\langle a|), \]

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

The stochastic solvation coordinate,

\[ U(t) \equiv e^{ihat/h}Ue^{-ihat/h}e^{ihat/h}(h_b - h_a)e^{-ihat/h}, \]

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

\[ \lambda = \langle U(t) \rangle \equiv \text{tr}[U(t)\rho_0^s] = \langle U \rangle, \]

and the solvation correlation function,

\[ C(t - \tau) = \langle [U(t) - \lambda][U(\tau) - \lambda] \rangle. \]

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 function,

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

Here, \( \Theta(t) \) is the Heaviside step function and \( \gamma^{-1} \equiv \tau_L = \tau_D(\varepsilon_\infty/\varepsilon_0) \), with \( \tau_D \) being the Debye time parameter, and \( \varepsilon_\infty, \varepsilon_0 \) the static (high-frequency) dielectric constant of the solvent. The corresponding solvation correlation function in the semiclassical high-temperature limit reads:

\[ C(t) \approx \lambda(2k_BT - i\hbar\gamma)e^{-\gamma t}. \]

For this model, the exact reduced density matrix dynamics has been constructed, in terms of excitations:

\[ \rho_n = -(iL + n\gamma)\rho_n - iB\rho_{n+1} - inA\rho_{n-1}; \quad n \geq 0, \]

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

\[ L\hat{O} \equiv \hbar^{-1}[H, \hat{O}], \]

\[ A\hat{O} \equiv \frac{2\lambda k_BT}{\hbar^2}||b||[b], \hat{O} - i\frac{\lambda T}{\hbar}||b||[b], \hat{O}, \]

\[ B\hat{O} \equiv ||b||[b], \hat{O]. \]

Here, \( ||\cdot|| \) denotes anticommutator. It has been shown24 that the individual auxiliary operator \( \rho_{n+1} \) accounts for the \( 2n^{th} \)-order system-bath interaction contribution to the reduced dynamics of the primary interested \( \rho \); see also the comments in the last paragraph of Sec. II B.

B. Continued fraction Green’s function formalism

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

\[ \rho_n(t) \equiv e^{-n\gamma t}\mathcal{U}_n(t)(\rho(0)); \quad \mathcal{U}_n(0) = \delta_{n0}. \]

Equations (11) read now

\[ \mathcal{U}_n(t) = -iL\mathcal{U}_n(t) - iBe^{-\gamma t}\mathcal{U}_{n+1}(t) - inAe^{\gamma t}\mathcal{U}_{n-1}(t), \]

which in the Laplace-domain are

\[ (s + iL)\hat{\mathcal{U}}_n(s) + iB\hat{\mathcal{U}}_{n+1}(s + \gamma) + inA\hat{\mathcal{U}}_{n-1}(s - \gamma) = \delta_{n0}. \]

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

\[ \hat{U}_0(s) \equiv G^{(0)}(s) \equiv G(s), \]

\[ \hat{U}_n(s) \equiv -inG^{(n)}(s)\hat{\mathcal{U}}_{n-1}(s - \gamma); \quad n > 0. \]
These equations will lead to
\[ G^{(n)}(s) = \frac{1}{s + iL + \Pi^{(n)}(s)}; \quad n \geq 0, \quad (16a) \]
with
\[ \Pi^{(n)}(s) \equiv (n + 1)BG^{(n+1)}(s + \gamma)A. \quad (16b) \]
The above equations, which can be recast as
\[ \Pi^{(n)}(s) = B \frac{n + 1}{s + \gamma + iL + \Pi^{(n+1)}(s + \gamma)} A, \quad (17) \]
constitute the infinite continued fraction formalism for evaluating each individual \( \Pi^{(n)}(s) \) or \( G^{(n)}(s) \).

The Green’s function \( G^{(0)}(s) \equiv G(s) \) and its associated \( \Pi^{(0)}(s) \equiv \Pi(s) \) are of the primary interest. The former resolves the reduced density matrix evolution (cf. eq 15a and eq 17 with \( n = 0 \)),
\[ \dot{\rho}(s) = \int_0^\infty dt e^{-st} \rho(t) = G(s) \rho(0). \quad (18) \]
This equation can be recast as (cf. eq 16a at \( n = 0 \))
\[ s\dot{\rho}(s) - \rho(0) = -iL\dot{\rho}(s) - \Pi(s)\dot{\rho}(s), \quad (19) \]
which in the time-domain reads
\[ \dot{\rho}(t) = -iL\rho(t) - \int_0^t d\tau \Pi(t - \tau) \rho(\tau). \quad (20) \]
Therefore,
\[ \Pi(s) = \Pi^{(0)}(s) = \int_0^\infty dt e^{-st} \Pi(t), \quad (21) \]
represents the memory kernel in the Laplace domain.

The initial input for the inverse recursive evaluation of \( \Pi(s) \) (eq 17) can be chosen based on the following observation. Each \( A \) is of second order in the system-bath coupling; thus the leading contribution of \( \Pi^{(n)} \) to the required \( \Pi \) is of the \((2n)^{th}\) order. Moreover, as the mathematical nature of continued fraction, convergency is also guaranteed practically for arbitrary strength and timescale 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 an superoperator (or Liouville-space operator) \( \mathcal{O} \) is defined in the double-bracket notation as,\[ O_{jj',kk'} \equiv \langle jj'| \mathcal{O} | kk' \rangle, \quad (22) \]
so that
\[ \mathcal{O} = \sum_{jj',kk'} O_{jj',kk'} \langle jj' | (kk') \rangle. \quad (23) \]
For a two-level system considered in this work, each tensor has \( 2^4 = 16 \) elements. That \( \mathcal{O} \) is Hermite implies \( O_{jj',kk'} = O_{j'j,k'k} \). Apparently, all \( \Pi^{(n)} \) and \( G^{(n)} \) are Hermite.

To analyze the tensor elements of \( \Pi^{(n)} \) (eq 16), let us first examine \( A \) and \( B \), defined by eqs 12 and 26 respectively. They are found to be diagonal, with the nonzero elements of \( A_{ba,ba} = \lambda (2\kappa B T - i\hbar \gamma)/\hbar^2 \), \( A_{bb,bb} = -i2\lambda \gamma/\hbar \), and \( B_{ba,ba} = -B_{ab,ab} = 1 \). As results, the only nonzero elements in \( \Pi^{(n)} \) (eq 16a) are
\[ x(n) = \Pi_{ba,ba}^{(n)}, \quad y(n) = \Pi_{ba,ab}^{(n)}, \quad z(n) = \Pi_{ba,bb}^{(n)} \quad (24) \]
and their Hermitian conjugate elements, and they are related to the Green’s function tensor elements,
\[ X(n) = G_{ba,ba}^{(n)}, \quad Y(n) = G_{ba,ab}^{(n)}, \quad Z(n) = G_{ba,bb}^{(n)} \quad (25) \]
by [denoting \( \eta \equiv \lambda (2\kappa B T - i\hbar \gamma)/\hbar^2 \)]
\[ x(n) = \eta (n + 1) X^{(n+1)}(s + \gamma), \quad (26a) \]
\[ y(n) = -\eta^* (n + 1) Y^{(n+1)}(s + \gamma), \quad (26b) \]
\[ z(n) = (\eta - \eta^*) (n + 1) Z^{(n+1)}(s + \gamma). \quad (26c) \]

To evaluate the involving Green’s function elements via eq 16a, we apply the Dyson equation,
\[ \dot{G} = \dot{G} - G(iL' + \Pi')G, \quad (27) \]
with \( \dot{G} \) being the diagonal contribution, and \( L' \) and \( \Pi' \) the off-diagonal parts of the involving \( L \) and \( \Pi \) respectively. Here and in eqs 28 and 29 follows, 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
\[ \alpha \equiv s + (i/\hbar)(E^2 + \lambda) + x, \quad (29a) \]
\[ \beta \equiv s^{-1}(V/\hbar)^2(2 + i\hbar z/V). \quad (29b) \]

We have thus obtained 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 \( \Pi \) 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 \( \rho(s) \) [eq. 14], where \( \rho(t = 0) = [aa] \). By separating \( \rho(s) \) into population vector \( P = [\rho_{aa}, \rho_{bb}]^T \) and coherent vector \( [\rho_{ab}, \rho_{ba}]^T \) components, and then using eq. 19 to eliminate the latter, we obtain the ET kinetic equations in Laplace domain as

\[
s \dot{\rho}(s) - P(0) = K(s) \rho(s), \tag{30}\]

with

\[
K(s) = T_{pc}(s + T_{cc})^{-1} T_{cp} - T_{pp}. \tag{31}\]

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 eq. 19 respectively. Tensor analysis (cf. Sec. II C) results in \( T_{pp} = 0 \), and

\[
T_{cc} = iV \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}, \quad T_{cp} = T_{pc} + \begin{pmatrix} 0 & \Pi_{10,11}^s \\ 0 & \Pi_{10,11} \end{pmatrix}. \tag{32a}\]

\[
T_{cc} = i(E^o + \lambda) \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \Pi_{10,10}^s & \Pi_{10,01}^s \\ \Pi_{10,01} & \Pi_{10,10} \end{pmatrix}. \tag{32b}\]

Note that eq. 30 in time domain reads

\[
\dot{P}(t) = \int_0^t d\tau \dot{K}(t-\tau)P(\tau). \tag{33}\]

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

\[
\dot{P}_a(t) = -\int_0^t d\tau \dot{k}(t-\tau)P_a(\tau) + \int_0^t d\tau \dot{k}'(t-\tau)P_b(\tau). \tag{34}\]

The forward and backward rate equations are

\[
k(s) = -K_{aa}(s) = \int_0^\infty dt e^{-st} \dot{k}(t), \tag{35a}\]

\[
k'(s) = K_{ab}(s) = \int_0^\infty dt e^{-st} \dot{k}'(t). \tag{35b}\]

Together with eq. 31, eq. 32, and \( T_{pp} = 0 \), we obtain

\[
k(s) = \frac{2|V|^2}{\hbar^2} \text{Re} \frac{\alpha(s) + y(s)}{[\alpha(s)]^2 - |y(s)|^2}, \tag{36a}\]

and

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

Here \( \alpha(s) = s + (i/\hbar)(E^o + \lambda) + x(s) \) is the same as eq. 29a, while \( x = \Pi_{ba,ba} = x(0), y = \Pi_{ba,ab} = y(0), \) and \( z = \Pi_{ba,bb} = z(0) \) 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 of the inverse recursive evaluation of the \( \Pi(s) \) tensor elements had been detailed in Sec. II B and Sec. II 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 \( \gamma \)) limit, the present rate constant \( k \) (eq. 35 at \( s = 0 \)) recovers the celebrated Marcus’ ET rate expression of eq. 2. We shall also be interested in the reaction Gibbs free-energy, \( \Delta G^o = -k_B T \ln(k/k') \), entropy \( \Delta S^o = -\partial \Delta G^o/\partial T \), and enthalpy \( \Delta H^o = \Delta G^o + T \Delta S^o \). We shall demonstrate how the rate constants and reaction thermodynamics functions depend on the model parameters, reaction endothermicity \( E^o \), solvent reorganization energy \( \lambda \), and longitudinal relation 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 being further specified. In fact, the value of \( V \) may be considered as the unit that scales other parameters used. The temperature should also varies around \( T = 298 \) K in order to numerically evaluation of 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 the fast (\( \kappa \gg 1 \)) solvent modulation limit. For \( \lambda = 3 \) kJ/mol at \( T = 298 \) K, that \( \kappa = 1 \) corresponds to \( \tau_L = 16.5 \) fs, while the typical ET solvation correlation timescale is of picoseconds. We will show that the parameter \( \kappa \) can also be used in ET rate problem.

Figure 11 depicts ET rate \( k \) as the function of solvent relaxation time \( \tau_L = 1/\gamma \) at four representing values of endothermicity, \( E^o = 0, -1, -3 \), 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 \( E^o = 0 \) (symmetric case), the system is in Fermi resonance and the ET is dominant by coherent tunneling. The observed rate in this case exhibits the motional narrowing behaviors. The faster the solvent modulation is, the larger the coherent resonant tunneling rate will be. In a nonsymmetric (\( E^o \neq 0 \)) system, the barrier crossing is significant and the observed ET rate exhibits clearly the Kramers’ turnover behaviors.

The rates observed in the slow solvent modulation (large \( \tau_L \) which amounts to large viscosity) region of
Fig. 1 are closely related to the Marcus’ inversion behaviors. Figure 2 depicts the ET rate, in term of \(\ln(k/k_{\text{max}})\), as the function of reaction endothermicity \(E^\circ\), in the slow modulation region \((\tau_L = 10 \text{ ps})\), at two specified values of transfer coupling strength, \(V = 0.01\) and 1 kJ/mol. When the transfer coupling is small \((V = 0.01 \text{ kJ/mol})\), the rate in the slow solvent modulation regime does have the Marcus’ nonadiabatic form, \(\ln(k/k_{\text{max}}) = -(E^\circ + \lambda^2)/(4k_BT)\) of eq (2) cf. the thin-solid vs. thin-dash curves. In the case of \(V = 1 \text{ kJ/mol}\), however, the rate deviates significantly from the Marcus’ expression. The poorly-fitted parabolic function there, \(-E^\circ - E_{\text{max}}^2/(\zeta 4k_BT)\) (dash-curve), is found to be of \(E_{\text{max}}^\circ = -2.4 \text{ kJ/mol and } \zeta = 0.3\).

Figure 3 shows the 3d-plot of reaction Gibbs free-energy \(\Delta G^\circ\) as the function of \((\lambda, \tau_L)\), exemplified at \(T = 298 \text{ K}\) with \(E^\circ = -3 \text{ kJ/mol}\) and \(V = 1 \text{ kJ/mol}\). Reported in Fig. 4 are some representing 2d-slices of Fig. 3 for \(\Delta G^\circ\), together with the numerically evaluated reaction entropy \(\Delta S^\circ\) and enthalpy \(\Delta H^\circ\). The observed features here are listed as follows.

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

(ii) \(\Delta G^\circ\), \(\Delta H^\circ\) and \(E^\circ\) are of 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 \(\Delta G^\circ\) on \((\lambda, \tau_L)\), as shown in Fig. 3, is qualitatively similar to that in the weak transfer coupling regime;

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

(v) In the modest modulation regime \((\kappa \sim 1)\), the reaction thermodynamic functions \((\Delta G^\circ, \Delta H^\circ, \text{ and } \Delta S^\circ)\) exhibit certain nonlinear dependence on \((\lambda, \tau_L)\). In particular, the magnitudes of these ET reaction thermodynamic functions are of maximum values around \(\kappa \sim 1\) when \(\lambda > |E^\circ|\).

Interestingly, the observed Kramers’ turnover of rates occurs also around the \(\kappa \sim 1\) (intermediate friction) region. The relevant forward and backward rate constants are given in Fig. 5. This may at least partially account for the nonmonotonic 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. eqs 24 with eqs 21 and 23). For Debye solvents in which the solvation correlation is characterized by an exponential function (eq 10), the ET rates, or rate resolutions in general (eqs 36), can be evaluated readily via the inverse-recursion formalism (cf. eqs 21 with eqs 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 occur(s). This observation suggests the possibility of utilizing the thermodynamics data to extract such as the solvation correlation time parameter (cf. the left panel of Fig. 4).

This work has also developed a nonperturbative theory of reduced density matrix dynamics, in terms of continued fraction Green’s function (Sec. III B). This formalism can be used together with Dyson equation technique for efficient and analytical evaluation of reduced dynamics (Sec. III 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 \(k_BT \ll (|V|^2 + 1/2|E^\circ|^2)^{1/2}\). Generalization of the present continued fraction Green’s function approach to non-Debye solvents at arbitrary temperature is feasible and will be developed in future.

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

FIG. 2: The normalized rates, in the slow modulation regime ($\tau_L = 10$ ps), as the functions of $E^\circ$. The Marcus’ parabolic relation, $\ln(k/k_{\text{max}}) = -(E^\circ + \lambda)^2/(4k_B T \lambda)$, 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 neither fits well with a parabolic function (dash curve); see the text for details.

FIG. 3: Reaction Gibbs free-energy $\Delta G^\circ$ as the function of solvent parameters ($\lambda, \tau_L$), for an ET system with $E^\circ = -3$ kJ/mol and $V = 1$ kJ/mol at $T = 298$ K.

FIG. 4: Reaction thermodynamics functions $\Delta G^\circ$, $\Delta S^\circ$, and $\Delta H^\circ$: (a) as the functions of $\lambda$ at some selected values of $\tau_L$; (b) as the functions of $\tau_L$ at some selected values of $\lambda$. The ET system is same as that of Fig. 3.

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