Electron transfer dynamics: Zusman equation versus exact theory

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The Zusman equation has been widely used to study the effect of solvent dynamics on electron transfer reactions. However, application of this equation is limited by the classical treatment of the nuclear degrees of freedom. In this paper, we revisit the Zusman equation in the framework of the exact hierarchical equations of motion formalism, and show that a high temperature approximation of the hierarchical theory is equivalent to the Zusman equation in describing electron transfer dynamics. Thus the exact hierarchical formalism naturally extends the Zusman equation to include quantum nuclear dynamics at low temperatures. This new finding has also inspired us to rescale the original hierarchical equations and incorporate a filtering algorithm to efficiently propagate the hierarchical equations. Numerical exact results are also presented for the electron transfer reaction dynamics and rate constant calculations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3125003]

I. INTRODUCTION

Electron transfer (ET) reactions play important roles in many chemical and biological processes.1–3 During the ET processes, the nuclear degrees of freedom need to reorganize in responding to the change in charge distributions upon the electronic state transitions. The interplay of electronic coupling and nuclear reorganization dynamics could thus result in rich dynamical behaviors in ET reactions. A particular interesting example of nuclear dynamical effects on ET reaction is that, when increasing the nuclear relaxation time, ET reactions change from the nonadiabatic regime to the solvent-controlled adiabatic regime.1–15

A widely used approach to investigate the effect of solvent dynamics on ET reactions is the Zusman equation (ZE).4–8 In this equation, dynamics of the electronic degrees of freedom is coupled to a collective nuclear coordinate that subjects to overdamped dissipation. A major drawback of the ZE is that the nuclear degrees of freedom are described classically. Neglecting the quantum effects of nuclear dynamics in the ZE were found to yield unphysical results in particular parameter regimes, such as the violation of von Neumann condition,16,17 and negative ET rates.8,18 Even in the case of high temperature and small electronic coupling, Frantsuzov18 showed that the ZE gives unphysical results when the $|DG + \lambda|$ is large, where $\lambda$ is the reorganization energy, and $DG$ is the free energy difference.

To go beyond the ZE, one has to consider both the quantum enhancement of the fluctuation of the nuclear degrees of freedom, and more importantly, the non-Markovian dynamics of the collective solvent coordinate.8,17,18 Several ways to modify the ZE at low temperatures have been proposed.17,19–21 Ankerhold and Lehle19 and Zhang et al.20,21 derived generalized ZEs that can be applied to low temperature ET problems. Shi and Geva22 also proposed a non-Markovian modified ZE. However, the problems are not yet fully solved, and a general theory that can extend the ZE to low temperature cases is needed.

In this work, we apply the recently developed hierarchical equations of motion (HEOM) method23–33 to ET reactions to include the quantum effect of nuclear dynamics. The HEOM method was originally proposed by Tanimura and co-worker23,24 as a nonperturbative method to calculate the reduced system dynamics by extending Kubo’s stochastic Liouville equation method.34 We will show that, an early version of the HEOM,23 which is a high temperature approximation to the exact formalism, is completely equivalent to the ZE in describing ET reaction dynamics. Thus the exact HEOM can be regarded as a natural extension of the ZE to low temperatures. The quantum fluctuations are now incorporated by using the exact collective solvent correlation functions, and the non-Markovian effects are considered by going to a multidimensional description of the nuclear dynamics. This newly found relationship has also inspired us to rescale the original HEOM equations and apply an efficient filtering algorithm to propagate the hierarchical equations.35 The physical meaning of the rescaling and the filtering algorithm will also be discussed in this study.

Although the HEOM method is exact, it is computationally more demanding than the ZE, and the physical intuition in the latter is also rather appealing. So it is interesting to further investigate the validity range of the ZE, on the basis of the present exact theory. This subject had been studied...
previously by several authors.\textsuperscript{12,17-19} Especially, Thoss \textit{et al.}\textsuperscript{15} compared the ZE results with those obtained from the numerically exact self-consistent hybrid approach in a wide range of parameter regimes. Our current study will focus on results showing the importance of Markovity of the nuclear dynamics\textsuperscript{17,18,22} in determining the validity of the ZE.

The remainder of this paper is organized as follows. In Sec. II, we exploit the HEOM approach to a spin-boson model with Debye spectral density to derive the exact theory for ET reaction dynamics. With the Tanimura–Kubo’s stochastic variable approach,\textsuperscript{27} we show that the high temperature approximation of HEOM formalism is equivalent to the ZE. The physical meaning of an efficient filtering algorithm\textsuperscript{35} to propagate the HEOM is also presented. In Sec. III, we investigate the validity range of the ZE using the Markovity criterion, and present further numerical results to calculate ET rate constants using the exact HEOM method. Conclusions and discussions are made in Sec. IV.

II. THEORY

A. The HEOM method to ET dynamics

We will consider the spin-boson model,\textsuperscript{36,37} which is often used as a model for electron transfer reactions:

\[
H_T = V\sigma_z + \frac{E_0}{2}\sigma_z + \sum_i \left[ \frac{1}{2} p_i^2 + \omega_i^2 \left( x_i - \frac{c_i}{\omega_i} \sigma_z \right)^2 \right] = H + H_B + H' + \text{const},
\]

where \( H \) is the system Hamiltonian,

\[
H = V\sigma_x - \frac{E_0}{2}\sigma_z,
\]

\( H_B \) is the bath Hamiltonian

\[
H_B = \sum_i \frac{1}{2} p_i^2 + \sum_i \frac{1}{2} \omega_i^2 x_i^2,
\]

and \( H' \) couples the system and bath degrees of freedom,

\[
H' = -\sum_i c_i x_i \otimes \sigma_z = -\mathcal{F} \otimes \frac{\sigma_z}{2},
\]

\( \sigma_z = |1\rangle\langle 1| + |2\rangle\langle 2| \) and \( \sigma_x = |1\rangle\langle 1| - |2\rangle\langle 2| \) are the Pauli matrices; \( x_i \) and \( p_i \) are the mass-weighted position and momentum of the \( i \)th phonon bath mode with frequency \( \omega_i \); and \( F = 2\sum_i c_i x_i \) is the collective bath coordinate that directly couples to the electronic degree of freedom. Throughout this paper, we set \( \hbar = 1 \), and \( \beta = 1/(k_B T) \).

The interacting spectral density of the harmonic bath is defined as

\[
\lambda = 4 \pi \int_0^\infty d\omega \frac{J(\omega)}{\omega}.
\]

The correlation function of the collective bath coordinate \( F \) is related to the spectral density via the fluctuation dissipation theorem:\textsuperscript{37}

\[
C(t) = \frac{1}{Z_B} \text{Tr} (e^{-\beta H_B} e^{iH_F} F e^{-iH_F} F) = 4 \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} J(\omega)}{1 - e^{-\beta \omega}}.
\]

Here, \( Z_B = \text{Tr} e^{-\beta H_B} \) is the partition function of the uncoupled harmonic bath.

For the Debye spectral density

\[
J(\omega) = \frac{\eta \gamma_{\omega}}{\omega^2 + \gamma^2},
\]

the reorganization energy \( \lambda = 2\eta \), and \( C(t) \) in Eq. (7) can be written into a sum of exponential decaying functions in time:

\[
C(t > 0) = \sum_{k=0}^{\infty} c_k e^{-\gamma t}.
\]

We assume a product initial state \( \rho_I(0) = \rho(0) \otimes e^{-\beta H_B}/Z_B \) for the total system. The HEOM can be derived using the path integral technique,\textsuperscript{23-28,31,38,39} or the stochastic Liouville equation approach.\textsuperscript{35,40,41} The final results can be written as

\[
\dot{\rho}_n = -\left( i\mathcal{L} + \sum_k n_k \gamma_k \right) \rho_n - i \left[ \frac{\sigma_z}{2} \sum_k \rho_{n^k}^* - \frac{\sigma_z}{2} \rho_n \right] - i \sum_k \left[ c_k \left( \frac{\sigma_z}{2} \rho_{n^k} - c_k \rho_n \right) \right],
\]

where \( \mathcal{L} \rho = [H, \rho] \), and \( \rho_0 = \rho \) is the reduced system density operator of primary interest. The subscript \( n = \{ n_k \} = \{ n_0, n_1, \cdots \} \) denotes the lowest power dependences of individual exponential terms in \( C(t) \) of Eq. (9) on the specified auxiliary density operator (ADO) \( \rho_n \). The subscript \( n_k^c \) differs from \( n_k \) only by changing the specified \( n_k \) to \( n_{k+1} \).

B. Relation to the Zusman equation

The Debye spectral density [Eq. (8)] describes a Markovian bath environment to the collective bath coordinate \( F \) in the high temperature limit.\textsuperscript{23,24,27} In such cases, we can use the classical approximation for the real part of \( C(t) \) [cf. Eqs. (9)–(11)], which gives
\begin{equation}
\langle F(t)F(0) \rangle = \lambda (2k_B T - i \gamma) e^{-\beta \gamma \rho_n(t)},
\end{equation}

This approximation holds for \( \beta \gamma \ll 1 \), and leads to the approximate HEOM in the form of \(^{14}\)

\begin{equation}
\dot{\rho}_n(t) = -\left( i\mathcal{L} + n \gamma \right) \rho_n(t) - inA\rho_{n-1}(t) - iB\rho_{n+1}(t),
\end{equation}

where

\begin{equation}
A\rho = 2\lambda k_B T[ \sigma_2/2, \rho] - i \lambda \gamma [ \sigma_2/2, \rho],
\end{equation}

\begin{equation}
B\rho = [ \sigma_2/2, \rho].
\end{equation}

Now we denote

\begin{equation}
\rho_n(t) = \begin{bmatrix}
a_n(t) & c_n(t) + id_n(t) \\
c_n(t) - id_n(t) & b_n(t)
\end{bmatrix},
\end{equation}

and recast Eq. (14) in terms of these real variables. After some simple algebra, we obtain

\begin{equation}
\begin{aligned}
\dot{a}_n &= -n \gamma a_n - n \lambda \gamma a_{n-1} - 2Vd_n,
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\dot{b}_n &= -n \gamma b_n + n \lambda \gamma b_{n-1} + 2Vd_n,
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\dot{c}_n &= -n \gamma c_n - E_0d_n + d_{n+1} + 2n \lambda k_B Tc_{n-1},
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\dot{d}_n &= -n \gamma d_n + E_0c_n - c_{n+1} - 2n \lambda k_B Tc_{n+1} + V(a_n - b_n).
\end{aligned}
\end{equation}

(18d)

With each \( \rho_n(t) \) in Eq. (17) being rescaled properly (see below), the above set of equations is just the ZE expanded in a proper basis set, as constructed previously. \(^{7,8}\)

To better understand the physical meaning of Eq. (14), we will follow the stochastic variable method used by Tanimura and Kubo \(^{23,27}\) to proceed with the derivation of the ZE. For this purpose, we first set

\begin{equation}
\tilde{\rho}_n(t) = (2\lambda k_B T)^{-n/2} \rho_n(t),
\end{equation}

and recast Eq. (14) as

\begin{equation}
\begin{aligned}
\dot{\tilde{\rho}}_n(t) &= -\left( i\mathcal{L} + n \gamma \right) \tilde{\rho}_n(t) - i\sqrt{2\lambda k_B T} \left[ \frac{\sigma_2}{2}, \tilde{\rho}_{n+1}(t) \right] \\
&\quad + n\tilde{\rho}_{n-1}(t) \right) - \frac{\lambda \gamma}{\sqrt{2\lambda k_B T}} \left[ \frac{\sigma_2}{2}, n\tilde{\rho}_{n-1}(t) \right].
\end{aligned}
\end{equation}

(20)

We shall show that Eq. (20) is nothing but a basis expansion of the following equation: \(^{4,6,7}\)

\begin{equation}
\begin{aligned}
\frac{\partial}{\partial t} \rho_0(\Omega, t) &= -\left( i\mathcal{L} + \Gamma_\Omega \right) \rho_0(\Omega, t) - i\sqrt{2\lambda k_B T} \left[ \frac{\sigma_2}{2}, \rho_0(\Omega, t) \right] \\
&\quad + \frac{\lambda \gamma}{\sqrt{2\lambda k_B T}} \left[ \frac{\sigma_2}{2}, (n + 1) \rho_0(\Omega, t) \right].
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\omega \rho_0(\Omega, t) &= -\left( i\mathcal{L} + \Gamma_\Omega \right) \rho_0(\Omega, t) - i\sqrt{2\lambda k_B T} \left[ \frac{\sigma_2}{2}, \rho_0(\Omega, t) \right] \\
&\quad + \frac{\lambda \gamma}{\sqrt{2\lambda k_B T}} \left[ \frac{\sigma_2}{2}, (n + 1) \rho_0(\Omega, t) \right].
\end{aligned}
\end{equation}

Here, \( \Omega \) is a classical stochastic variable, and

\begin{equation}
\Gamma_\Omega = -\gamma \frac{\partial}{\partial \Omega} \left( \Omega + \frac{\partial}{\partial \Omega} \right).
\end{equation}

(22)

The equivalence between Eqs. (20) and (21) can be formally established via

\begin{equation}
\rho_0(\Omega, t) = \sum_{n=0}^{\infty} \frac{1}{\sqrt{n!}} \tilde{\rho}_n(t) \phi_n(\Omega),
\end{equation}

where \( \phi_n(\Omega) \) is the right eigenfunction of the operator \( \Gamma_\Omega \), i.e.,

\begin{equation}
\phi_n(\Omega) = e^{-\Omega^2/4} \phi_{n_{\text{bar}}}(\Omega),
\end{equation}

with \( \phi_{n_{\text{bar}}}(\Omega) \) being the normalized harmonic eigenfunctions.

In particular, \( \phi_{0_{\text{bar}}}(\Omega) = (2\pi)^{-1/2} e^{-\Omega^2/4} \). The reduced system density operator can thus be evaluated as \( \rho(\Omega, t) = \tilde{\rho}_0(t) = \sum_{n=0}^{\infty} \int d\Omega \rho_0(\Omega, t) = \frac{2\pi^{1/2}}{\pi^{1/4}} d\Omega \rho(\Omega, t). \)

The equivalence between Eqs. (20) and (21) is verified in detail as follows. We start with the eigenvalue problem of \( \Gamma_\Omega \) [Eq. (22)]. It can be readily solved using the following transform:

\begin{equation}
e^{\Omega^2/4} \Gamma_\Omega e^{-\Omega^2/4} = \gamma \frac{\Omega^2}{4} - \frac{\partial^2}{\partial \Omega^2} - \frac{1}{2} = \gamma a_\Omega^0 \hat{a}_\Omega,
\end{equation}

(25)

with

\begin{equation}
\hat{a}_\Omega = \Omega + \frac{\partial}{\partial \Omega}, \quad \hat{a}_\Omega^0 = \frac{\Omega}{2} - \frac{\partial}{\partial \Omega},
\end{equation}

(26)

satisfying \([\hat{a}_\Omega, \hat{a}_\Omega^0] = 1\). Thus, \( \phi_n(\Omega) \) of Eq. (24) does constitute the right eigenfunction of \( \Gamma_\Omega \), with

\begin{equation}
\Gamma_\Omega \phi_n(\Omega) = n \gamma \phi_n(\Omega).
\end{equation}

(27)

To be convenient, we denote \( \tilde{\phi}_n(\Omega) = (1/n) \phi_n(\Omega) \), so that Eq. (23) becomes \( \rho(\Omega, t) = \sum_{n=0}^{\infty} \tilde{\rho}_n(t) \tilde{\phi}_n(\Omega) \), in the following derivation. From Eq. (27), we obtain therefore

\begin{equation}
\sum_{n=0}^{\infty} n \gamma \tilde{\rho}_n(t) \tilde{\phi}_n(\Omega) = \Gamma_\Omega \rho(\Omega, t).
\end{equation}

(28)

Furthermore, using the standard relations, \(^{29a, b}\)

\begin{equation}
\Gamma_\Omega \phi_{n_{\text{bar}}}(\Omega) = \sqrt{n} \phi_{n_{\text{bar}}}(\Omega),
\end{equation}

\begin{equation}
\Gamma_\Omega \phi_{n_{\text{bar}}}(\Omega) = \sqrt{n + 1} \phi_{n_{\text{bar}}}(\Omega),
\end{equation}

we obtain \( \Omega \phi_n = \sqrt{n} \phi_{n-1} + \sqrt{n + 1} \phi_{n+1} \), or

\begin{equation}
\Omega \tilde{\phi}_n(\Omega) = \tilde{\phi}_{n-1}(\Omega) + (n + 1) \tilde{\phi}_{n+1}(\Omega).
\end{equation}

(30)

It leads to [we have used the notation that \( \tilde{\phi}_{-1}(\Omega) = 0 \)]

\begin{equation}
\sum_{n=0}^{\infty} \left[ \tilde{\rho}_{n+1}(t) + n \tilde{\rho}_{n-1}(t) \right] \tilde{\phi}_n(\Omega)
\end{equation}

\begin{equation}
\begin{aligned}
&= \sum_{n=0}^{\infty} \tilde{\rho}_n(t) \left[ \tilde{\phi}_{n-1}(\Omega) + (n + 1) \tilde{\phi}_{n+1}(\Omega) \right] = \Omega \rho(\Omega, t).\end{aligned}
\end{equation}

(31)

Similarly, we obtain also \( \partial / \partial \Omega \) \( \phi_n = -\sqrt{n + 1} \phi_{n+1} \), or

\begin{equation}
\frac{\partial}{\partial \Omega} \tilde{\phi}_n(\Omega) = - (n + 1) \tilde{\phi}_{n+1}(\Omega).
\end{equation}

(32)

It results in
The equivalence between the approximated HEOM [Eq. (20)] and the ZE [Eq. (21)] via Eq. (23) is now established explicitly, by using Eqs. (28), (31), and (33). The above derivation follows basically the method of Tanimura and Kubo, except that the present (33) differs from the previous result. In this approximation, we have recently proposed an efficient filtering algorithm for the numerical propagation, which automatically truncates the hierarchy levels $L$ on the fly with a preselected error tolerance. The filtering method is base on a proper rescaling,

$$
\tilde{\rho}_n(t) = \left( \prod_k \left| c_k \right|^2 \! n_k \right)^{1/2} \rho_n(t),
$$

so that Eq. (12) with the Ishizaki–Tanimura truncation [Eq. (36)] reads

$$
\tilde{\rho}_n = -\left( i \mathcal{L} + \delta R + \sum_{k=0}^K n_k \gamma_k \right) \tilde{\rho}_n - i \sum_{k=0}^K \sqrt{(n_k+1)} |c_k|^2 \left( \sigma_\epsilon \tilde{\rho}_n^* - \sigma_\epsilon \tilde{\rho}_n \right),
$$

where $\delta R = \Delta_k [(\sigma_\epsilon/2), [(\sigma_\epsilon/2), \rho]]$, with

$$
\Delta_k = \sum_{m=1}^\infty \frac{c_{km}}{\gamma_k \gamma_m} = \frac{4 \eta k_B T}{m} - \sum_{k=0}^K \frac{c_k}{\gamma_k}.
$$

The scaled ADOs, $\tilde{\rho}_n(t)$, are all dimensionless, decay to zero for high hierarchical levels, and have a uniform error tolerance. To explain this more clearly, we consider the simplified case with the high temperature semiclassical approximation described in Sec. II B. In that case, Eq. (37) amounts to $\tilde{\rho}_n(t) = \left( 1/\sqrt{n} \right) \tilde{\rho}_n(t)$ (except for using only the real part of $c_0$ for the scaling in Sec. II B), which is associated more naturally with the normalized basis set $\phi_n(\Omega)$ in Eq. (23). Since $\phi_n(\Omega)$ is more oscillatory as $n$ increases, the expansion coefficient $\tilde{\rho}_n(t)$ should become small when $n$ is sufficiently large.

The accuracy-controlled filtering method to safely discard unimportant ADOs (Ref. 35) is implemented in the following way: at each time step, those $\tilde{\rho}_n$, whose largest absolute value of all the matrix elements is smaller than the preset error tolerance, are discarded. Converged numerical result from Eq. (38) is obtained by varying $K$ and the preset error tolerance. In this way, the anchor level $L$ of the hierarchy is determined automatically on the fly and the number of ADOs during the numerical propagation is reduced significantly.

III. RESULTS

A. Preliminary insights

As shown in previous studies, the ZE will give unphysical ET rates at large reorganization energy. Figure 1 presents such an example where the ZE fails. The parameters used are $\beta \gamma = 1$, $\beta V = 0.1$, $E_0 = 0$, and $\beta \Delta = 20$. It can be seen that the HEOM result gives correct rate dynamics while the ZE give negative rate constants and violates the positivity of reduced dynamics.

Since the spin-boson model with a Debye spectral density has been previously studied using the self-consistent hybrid method, we also test our numerical algorithm with several previously investigated models. Figures (a)-(c)
present the examples in the nonadiabatic, adiabatic, and intermediate regimes. The parameters are the same as those used in Ref. 12: \( \gamma / V = 0.25, \beta V = 5, \eta / V = 5; \) (b) \( \gamma / V = 5, \beta V = 0.5, \eta / V = 10; \) (c) \( \gamma / V = 1, \beta V = 1, \eta / V = 5. \) The results shown in Fig. 2 are consistent with those obtained in Ref. 12.

**B. Validity range of the Zusman equation**

Although the ZE is usually derived using the high temperature approximation, i.e., \( \beta \gamma \ll 1, \) this condition were found not able to determine its real validity range. For example, it could fail at relatively high temperatures,\(^{18}\) but works well in several low temperature problems [see, e.g., Fig. 3(a) and Fig. 7 of Ref. 12] when the reorganization energy is small.

A more important criterion that has been brought out is that the validity of the ZE depends on whether the dynamics of the collective solvent coordinate \( F \) can be treated using the Markovian approximation.\(^{18,22}\) Note that this should be differentiated from the Markovian approximation to derive the reduced dynamics for the electronic degree of freedom only. Shi and Geva\(^{22}\) showed that the ZE is valid to calculate the electronic dynamics even at low temperatures, whenever the Markovian approximation can be applied, despite of the fact that the quantum effect of the nuclear degrees of freedom is not described correctly in such cases. Since the first Matsubara term have the time scale of \( \beta \), a crude but useful criterion for the Markovian approximation to hold is given by \( \gamma / V \ll \omega_0, \) where \( \omega_0 \) is the system characteristic frequency determined by \( \lambda, E_0, \) and \( V. \) We will consider some examples to further illustrate the usefulness of the Markovian criterion, as follows.
rrium populations are needed in the following rate calculation. For the special case of zero bias $E_0=0$, $P_0^1=P_0^2=0.5$. When $E_0 \neq 0$, they can be obtained using imaginary time path integral approaches.\textsuperscript{42,43}

To calculate $k_f$, we set the initial density operator for the whole system $\rho(t)=|1\rangle\langle 1| \otimes e^{-\beta H_B}/Z_B$. The electronic coupling is first turned off during a period of simulation, by setting $V=0$, to allow the total system getting equilibrated on the donor state. It is then turned on for further propagation. We then follow the population dynamics $P_1(t)$ and $P_2(t)$ till the total $k_f+k_b$, defined in $\dot{P}_1(t) - \dot{P}_2(t) = -(k_f+k_b)[(P_1(t) - P_2(t)] -(P_2(t)-P_2(t))]$, reaches a plateau after a short initial relaxation time. The forward rate constant $k_f$ is then determined by using the detailed balance relation.

In the calculations below, converged results were obtained with the number of Matsubara frequencies $K$ up to 16, and the maximum automatically truncated hierarchical levels up to 40. The forward ET reaction rates were calculated using the HEOM, the ZE, and also the Fermi golden rule (FGR) result,\textsuperscript{37}

$$k_{\text{FGR}} = 2V^2 \Re \int_0^\infty dt e^{-i\omega t} \exp \left[ -\int_0^\infty d\omega \frac{4J(\omega)}{\pi \omega^2} \times \{ \coth(\beta \omega/2) \{ 1 - \cos(\omega t) \} - i \sin(\omega t) \} \right]. \quad (41)$$

Figure 5 shows the temperature effect on ET rates for $\gamma=V$, $E_0=0$, and $\lambda=10V$, when $\beta V$ varies from 0.025 to 3. It can be seen that the rate from the ZE agrees well with the exact result at low temperatures and deviates from the exact result at high temperatures. The Zusman rate constant finally becomes negative at $\beta V=2$, giving unphysical results.

Figure 6 shows the ET rates for different reorganization energies, using the parameters $\beta \gamma=0.5$, $E_0=0$, and $\gamma/V=1$. In the parameter region $0<\lambda/V<2.2$, the ET dynamics is coherent, and a rate constant cannot be defined. It can be seen that the ZE works well for small reorganization energies, but getting poorer as the reorganization energy increases.

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In the calculations below, converged results were obtained with the number of Matsubara frequencies $K$ up to 16, and the maximum automatically truncated hierarchical levels up to 40. The forward ET reaction rates were calculated using the HEOM, the ZE, and also the Fermi golden rule (FGR) result,\textsuperscript{37}

$$k_{\text{FGR}} = 2V^2 \Re \int_0^\infty dt e^{-i\omega t} \exp \left[ -\int_0^\infty d\omega \frac{4J(\omega)}{\pi \omega^2} \times \{ \coth(\beta \omega/2) \{ 1 - \cos(\omega t) \} - i \sin(\omega t) \} \right]. \quad (41)$$

Figure 5 shows the temperature effect on ET rates for $\gamma=V$, $E_0=0$, and $\lambda=10V$, when $\beta V$ varies from 0.025 to 3. It can be seen that the rate from the ZE agrees well with the exact result at low temperatures and deviates from the exact result at high temperatures. The Zusman rate constant finally becomes negative at $\beta V=2$, giving unphysical results.

Figure 6 shows the ET rates for different reorganization energies, using the parameters $\beta \gamma=0.5$, $E_0=0$, and $\gamma/V=1$. In the parameter region $0<\lambda/V<2.2$, the ET dynamics is coherent, and a rate constant cannot be defined. It can be seen that the ZE works well for small reorganization energies, but getting poorer as the reorganization energy increases.
the HEOM approach used in this paper is that its efficiency in studying nonequilibrium dynamics, as well as dissipative dynamics. The latter provides an exact solution to the ET dynamics, by taking into account both the quantum fluctuations of the collective bath coordinate and its non-Markovian dynamics. The physical meaning of the newly developed efficient alternative in such cases.

IV. CONCLUSION

The ZE provides an intuitive way to study the effect of solvent dynamics on ET reaction dynamics. However, its application is limited because of the neglect of quantum effects in describing the dynamics of the nuclear degrees of freedom. In this paper we derive the ZE as a high temperature approximation to the exact theory, the HEOM formalism. The latter provides an exact solution to the ET dynamics, by taking into account both the quantum fluctuations of the collective bath coordinate and its non-Markovian dynamics. The physical meaning of the newly developed efficient filtering algorithm to propagate HEOM is also illustrated.

We have also tested the validity range of the ZE using numerical exact results, and proposed that the validity of the ZE depends on whether the dynamics of the collective solvent coordinate can be treated using the Markovian approximation.

Since the HEOM method is based on nonperturbative propagation of the reduced density matrix, it can be used to study nonequilibrium dynamics, as well as dissipative dynamics under a driving laser field interaction. A drawback of the HEOM approach used in this paper is that its efficiency depends heavily on how quickly the expansion using Matsubara frequencies converges. At the lower temperature ($T \rightarrow 0$) limit, the expansion in Eqs. (9)–(11) hardly converges, and more efficient numerical approaches are needed. The mixed stochastic-HEOM method may provide an efficient alternative in such cases.

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