Hierarchical quantum master equation with semiclassical Drude dissipation

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We propose a nonperturbative quantum dissipation theory, in term of hierarchical quantum master equation. It may be used with a great degree of confidence to various dynamics systems in condensed phases. The theoretical development is rooted in an improved semiclassical treatment of Drude bath, beyond the conventional high temperature approximations. It leads to the new theory a simple modification but important improvement over the conventional stochastic Liouville equation theory, without extra numerical cost. Its broad range of validity and applicability is extensively demonstrated with two–level electron transfer model systems, where the new theory can be considered as the modified Zusman equation. We also present a criterion, which depends only on the system–bath coupling strength, characteristic bath memory time, and temperature, to estimate the performance of the hierarchical quantum master equation.

I. INTRODUCTION

Dissipation is often inevitable and plays important roles in many systems. The key quantity in quantum dissipation theory (QDT) is the reduced system density operator, \( \rho(t) \equiv \text{tr}_B \rho_{\text{total}}(t) \); i.e., the trace of total composite one over bath subspace. For Gaussian bath, exact QDT can be formulated with path integral1,2 or its differential version in terms of hierarchical equations of motion (HEOM).3–6,8,9,10,11,12,13,14,15,16,17 However, exact approaches are numerically expensive in general. In this paper, we propose an approximate HEOM theory, which will be termed hereafter as hierarchical quantum master equation (HQME). Compared with the traditional high-temperature approximation (HTA) schemes such as the stochastic Liouville equation,4–7 the new method requires about the same numerical effort, but enjoys a greatly improved range of validity. Moreover, the HQME supports also a convenient and versatile criterion of applicability that seems to be rather insensitive to specific systems.

We will exemplify the validity and applicability of the present theory with the standard electron transfer spin–boson model system. In this case, the HQME is analytically solvable, and its high–temperature limit is just the celebrated Zusman equation (ZE).22,23,24,25 The ZE treats the effect of bath via a diffusive solvation coordinate. Its validity has been a subject of study for years.26,27,28,29,30,31,32,33,34,35 With the aid of analytical solutions, we can now readily exploit the range of validity for both HQME and ZE, over the full parameters space of electron transfer systems.

The present development is rooted in an improved semiclassical treatment of the fluctuation–dissipation theorem. Consider a Gaussian stochastic bath variable \( F_B(t) \). It can be the fluctuating solvation coordinate \( U(t) - \langle U \rangle_B \) in electron transfer systems, or the fluctuating transition frequency \( \delta \omega_{eg}(t) - \langle \delta \omega_{eg} \rangle_B \) in spectroscopy. Its effect on system is completely described by the bath correlation function, \( C(t) \equiv \langle F_B(t) F_B(0) \rangle_B \). The classical Gaussian–Markovian description assumes

\[
C(t) = 2\lambda k_B T e^{-\gamma t}.
\]  

Adopted is the classical fluctuation–dissipation relation, such as \( \langle U^2 \rangle_B - \langle U \rangle_B^2 \approx 2k_B T \langle U \rangle_B \). This model has been widely used, for example, in the spectroscopic motional narrowing problems.18,19,35 It also leads to the stochastic Liouville equation description of reduced system dynamics.4–18,19,20,21 However, it discards the imaginary part that is responsible for the spectroscopic Stokes shift or solvent reorganization. In other words, the classical bath correlation function does not consider the back action of system on bath. The conventional HTA scheme adopts

\[
C_{\text{HTA}}(t) = \lambda(2k_B T - i\gamma) e^{-\gamma t}.
\]  

Here, the imaginary part assumes no approximation in the Drude dissipation model, while the real part remains its classical form. This scheme does account for the back action of system on bath. However, the reduced system density matrix dynamics based on \( C_{\text{HTA}}(t) \) encounters rather often the positivity violation problem that was originally not suffered by that based on classical \( C(t) \).

The above two conventional schemes are the low–order approximations of fluctuation–dissipation theorem, together with the Drude bath spectral density model,

\[
J(\omega) = \frac{2\lambda\gamma \omega}{\omega^2 + \gamma^2}.
\]  

The exact fluctuation–dissipation theorem reads2

\[
C(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \ e^{-i\omega t} \frac{J(\omega)}{1 - e^{-\beta \omega}}.
\]
with $\beta = 1/(k_B T)$ being the inverse temperature. Consider the bosonic function in the expansion:

$$
\frac{1}{1 - e^{-\beta \omega}} = \frac{1}{\beta \omega} + \frac{1}{2} + \frac{\beta \omega}{12} + \mathcal{O}((\beta \omega)^3).
$$

(5)

The classical $C_{\text{sc}}(t)$ [Eq. (6)] uses only the lowest order expansion; the high-temperature $C_{\text{HTA}}(t)$ [Eq. (2)] includes also the second term.

The proposed HQME approach is based on the following semiclassical bath correlation function,

$$
C_{\text{sc}}(t) = C_{\text{HTA}}(t) - \frac{\lambda \gamma}{6 k_B T} [\gamma e^{-\gamma t} - 2 \delta(t)].
$$

(6)

It uses all the three lowest terms of Eq. (5), thus, improving over $C_{\text{HTA}}(t)$ by two orders in $\beta \omega$. Interestingly, the resulting HQME for reduced dynamics costs almost no additional numerical effort, but largely overcomes the aforementioned positivity problem. This remarkable feature will be exemplified in simple electron transfer systems, where the HTA limit of HQME has been shown to be equivalent to the ZE.

The remainder of paper is organized as follows. We present the HQME on the basis of $C_{\text{sc}}(t)$ [Eq. (6)], its stochastic Liouville equation description, and its continued fraction Green’s function theory, respectively, in the three subsections of Sec. II. The exact HEOM formalism based on $C(t)$ of Eq. (4) is briefed in Appendix. In Sec. III we consider the two-level electron transfer spin-boson model, in which the continued fraction Green’s function theory of HQME can be analytically resolved and also the ZE is recovered in the HTA limit. Exemplified with this model, numerical studies on validity will be exemplified in simple electron transfer systems, where the HTA limit of HQME has been shown to be equivalent to the ZE.

In this formalism, the reduced system density operator, $\rho(t) \equiv \rho_0(t)$, couples hierarchically with a set of well-defined auxiliary density operators $\{\rho_n(t)\}$. The hierarchical construction resolves not just system–bath coupling strengths but also memory time scales. Each $\rho_n$, having been scaled by the factor $\left(\frac{n!}{c_r^*}c_r^*\right)^{-1/2}$, if compared with Ref. 11 or Ref. 36, is now dimensionless and possesses a unified error tolerance as that of $\rho_0$. Thus, an efficient on-the-fly filtering algorithm that also automatically truncates the hierarchy can be applied.

Note that the exact HEOM formalism can be constructed in principle for arbitrary non-Markovian dissipation, see Appendix for the exact theory of Drude dissipation. There the bath correlation function $C(t)$ is expanded in Matsubara exponential series of the exact fluctuation–dissipation theorem [Eq. (4)]. The exact theory is generally expensive, even with the state-of-the-art numerical filtering algorithm. Apparently, the HQME [Eq. (10)] is numerically appealing, much more practical to large systems, if the effect of involving approximation can be assessed in advance. We shall discuss this issue later in Sec. IV and Sec. V.

II. THEORY

A. Hierarchical quantum master equation

Consider the total Hamiltonian in the form of

$$
H_T(t) = H + QF_0(t).
$$

(7)

Denote $\mathcal{L}\hat{O} = [H, \hat{O}]$ as the reduced system Liouvillian, and set $\hbar = 1$ throughout this paper. The last term of Eq. (7) is the system–bath coupling, in which the system operator $Q$ defines the dissipative mode, through which the stochastic bath operator or generalized Langevin force $F_0(t)$ acting on the system. Recast the semiclassical bath correlation function of Eq. (6) as

$$
C_{\text{sc}}(t) = (c_r - i c_i) e^{-\gamma t} + 2 \Delta \delta(t),
$$

(8)

where

$$
c_r = 2 \lambda k_B T - \gamma \Delta, \quad c_i = \lambda \gamma, \quad \Delta = \frac{\lambda \gamma}{6 k_B T}.
$$

(9)

The corresponding HQME can then be constructed via the standard calculus–on–path–integral algebra. It reads

$$
\dot{\rho}_n(t) = -(i\mathcal{L} + \delta R + n \gamma) \rho_n(t) - i\sqrt{n} A \rho_{n-1}(t) - i\sqrt{n+1} B \rho_{n+1}(t),
$$

(10)

with

$$
\delta R \hat{O} = \Delta [Q, \{Q, \hat{O}\}], \quad B \hat{O} = \sqrt{c_r} [Q, \hat{O}], \quad A \hat{O} = \left( c_r [Q, \hat{O}] - i c_i \{Q, \hat{O}\} \right) / \sqrt{c_r}.
$$

(11a)

(11b)

In this formalism, the reduced system density operator, $\rho(t) \equiv \rho_0(t)$, couples hierarchically with a set of well-defined auxiliary density operators $\{\rho_n(t)\}$. The hierarchical construction resolves not just system–bath coupling strengths but also memory time scales. Each $\rho_n$, having been scaled by the factor $\left(\frac{n!}{c_r^*}c_r^*\right)^{-1/2}$, if compared with Ref. 11 or Ref. 36, is now dimensionless and possesses a unified error tolerance as that of $\rho_0$. Thus, an efficient on-the-fly filtering algorithm that also automatically truncates the hierarchy can be applied.

B. Stochastic Liouville equation description

Note that the HQME [Eq. (10)] has basically the same mathematical form, and thus about the same numerical cost, as the conventional stochastic Liouville equation. The latter is based on the classical bath $C_{\text{cl}}(t)$ [Eq. (11)], and can be recovered from Eq. (10) by setting $c_i = \Delta = 0$. Thus, the HQME supports the same physical picture, as described by $\dot{\rho}(\Omega, t)$ in the stochastic Liouville equation, with the diffusive solvation variable $\Omega$ being introduced for the effect of bath. The reduced system density operator is evaluated via $\rho(t) = \int d\Omega \rho(\Omega, t)$. The HQME [Eq. (10)] resolves the stochastic description as

$$
\dot{\rho}(\Omega, t) = \sum_{n=0}^{\infty} \rho_n(t) \phi_n(\Omega),
$$

(12)
where $\phi_n(\Omega) = e^{-\Omega^2/2}\phi_{\text{har}}(\Omega)$, with $\phi_{\text{har}}(\Omega)$ being the normalized harmonic eigenfunction, is the right-eigenfunction of the diffusion operator.\(^{4,5}\)

$$\Gamma_\Omega = -\gamma \frac{\partial}{\partial \Omega} \left( \Omega + \frac{\partial}{\partial \Omega} \right). \quad (13)$$

With the same algebra of Ref.\(^{15}\), we can show that the HQME [Eq. \((10)\)] is equivalent to the following stochastic Liouville equation description,

$$\frac{\partial}{\partial t} \hat{\rho}(\Omega, t) = -(i\mathcal{L} + \delta \mathcal{R} + \Gamma_\Omega) \hat{\rho}(\Omega, t)$$
$$- i\frac{c_r}{\sqrt{|c_r|}} \left[ Q, \left( \Omega + \frac{\partial}{\partial \Omega} \right) \hat{\rho}(\Omega, t) \right]$$
$$+ i\frac{c_r}{\sqrt{|c_r|}} \left[ Q, \frac{\partial}{\partial \Omega} \hat{\rho}(\Omega, t) \right]$$
$$+ \frac{c_r}{\sqrt{|c_r|}} \left\{ Q, \frac{\partial}{\partial \Omega} \hat{\rho}(\Omega, t) \right\}. \quad (14)$$

In the classical bath limit (setting $\Delta = c_r = 0$), the above equation reduces to the conventional stochastic Liouville equation.\(^{4,18,19,20,21}\) We have therefore extended the stochastic Liouville equation to not just the HTA bath, but also the present improved semiclassical scheme. Moreover, for the spin–boson system, the HTA ($\Delta = 0$) version of Eq. \((14)\) has been recently shown\(^\text{15}\) to be identical to the Zusman equation (ZE).\(^{22,21,24,25}\) Therefore, Eq. \((10)\) or Eq. \((14)\) can also be considered as a generalized and modified ZE to arbitrary systems, with much improved validity range of parameters; see Sec.\(^\text{IV}\) for a thorough demonstration.

### C. Continued fraction Green’s function formalism

The HQME formalism can in general apply to the systems in the presence of external time–dependent field driving. In this case, the initial conditions to Eq. \((10)\) are the steady–states $\{\rho_n(t=0) = \rho_n^0\}$ before the external field driving. This initial conditions can be evaluated by setting $\hat{\rho}_n = 0$, leading to Eq. \((10)\) a set of linear equations, under the constraint of $\tr\rho_0 = 1$. It results in $\rho_n(t=0) \neq 0$ generally, due to the initial system–bath coupling.

For the population transfer systems to be studied in the absence of external field driving, we set the initial state to be $\rho_n(t=0) = \rho(0)\delta_{n0}$. This corresponds to the initial total density matrix factorization ansatz. In this case, the HQME [Eq. \((10)\)] can be formally resolved with a continued fraction Green’s function formalism.\(^{4,5,7,11,25}\) Following the same procedure as Ref.\(^\text{36}\), we introduce the hierarchical Liouville–space propagators $\{\mathcal{U}_{n\geq0}(t)\}$ via

$$\rho_n(t) = e^{-\gamma t} \mathcal{U}_n(t) \rho(0); \quad \text{with} \quad \mathcal{U}_n(0) = \delta_{n0}. \quad (15)$$

and recast Eq. \((10)\) as (setting $i\mathcal{L}' = i\mathcal{L} + \delta \mathcal{R}$)

$$\mathcal{U}_n(t) = -i\mathcal{L}' \mathcal{U}_n(t) - i\sqrt{n} A e^{-i\mathcal{L}/'}(0) \mathcal{U}_{n-1}(t)$$
$$- i\sqrt{n} + 1 B \mathcal{U}_{n+1}(t). \quad (16)$$

In the Laplace domain, we have

$$\delta_{n0} = (s + i\mathcal{L}') \mathcal{U}_n(s) + i\sqrt{n} A \mathcal{U}_{n-1}(s - \gamma)$$
$$+ i\sqrt{n} + 1 B \mathcal{U}_{n+1}(s + \gamma). \quad (17)$$

Define the hierarchical Liouville–space Green’s functions $\{\mathcal{G}^{(n)}(s)\}$ via

$$\mathcal{U}_0(s) \equiv \mathcal{G}^{(0)}(s)$$
$$\mathcal{U}_n(s) \equiv -i\sqrt{n} \mathcal{G}^{(n)}(s) A \mathcal{U}_{n-1}(s - \gamma); \quad n > 0. \quad (18)$$

Then Eq. \((17)\) leads to

$$\mathcal{G}^{(n)}(s) = \frac{1}{s + i\mathcal{L}' + \Pi^{(n)}(s)}$$
$$\Pi^{(n)}(s) = (n + 1) B \mathcal{G}^{(n+1)}(s + \gamma). \quad (19)$$

The above equations constitute the continued fraction formalism to evaluate each individual $\Pi^{(n)}(s)$ or $\mathcal{G}^{(n)}(s)$.

Note that $\mathcal{G}^{(0)}(s) \equiv \mathcal{G}(s)$ and its associated $\Pi^{(0)}(s) \equiv \Pi(s)$ are the primary Green’s function and dissipation kernel resolution, respectively. The reduced density operator $\hat{\rho}(s) = \mathcal{G}(s)\rho(0)$ satisfies

$$s\hat{\rho}(s) - \rho(0) = -i\mathcal{L}'\hat{\rho}(s) - \Pi(s)\hat{\rho}(s), \quad (20)$$

which in the time domain reads

$$\hat{\rho}(t) = -i\mathcal{L}'\hat{\rho}(t) - \int_0^t d\tau \Pi(t - \tau)\hat{\rho}(\tau). \quad (21)$$

This is nonperturbative quantum master equation, with $\Pi(t - \tau) \equiv [\Pi(s)\big|_{s = t - \tau}]$ evaluated nonperturbatively via the continued fraction formalism and $i\mathcal{L}' \equiv i\mathcal{L} + \delta \mathcal{R}$.

To obtain the kinetic rate equations, we start with Eq. \((20)\) and formally eliminate the coherence components of the reduced density matrix, resulting in

$$s\hat{P}(s) - \hat{P}(0) = K(s)\hat{P}(s). \quad (22)$$

Its time–domain counterpart reads

$$\dot{\hat{P}}_j(t) = \sum_k \int_0^t d\tau K_{jk}(t - \tau)\hat{P}_k(\tau), \quad (23)$$

where $K_{jk}(s)$ are transfer rates resolutions for the transition from the state $k$ to the state $j$. They can be obtained via

$$K(s) = T_{PC}(s + T_{CC})^{-1}T_{CP} - T_{PP}. \quad (24)$$

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, respectively, defined by Eq. \((20)\) in a given representation.
III. ANALYTICAL RESOLUTION OF ELECTRON TRANSFER DYNAMICS

Consider hereafter the standard electron transfer model system. The total system–plus–bath composite Hamiltonian assumes $H_T = h_a|a⟩⟨a| + (h_b + E^o)|b⟩⟨b| + V(|a⟩⟨b| + |b⟩⟨a|)$. Here, $E^o$ denotes the reaction endothermicity, and $V$ is the transfer coupling matrix element that is assumed independent of the solvent degrees of freedom; $h_a$ or $h_b$ is the solvent Hamiltonian for the system in the donor $|a⟩$ or acceptor $|b⟩$ state, respectively. Their difference defines the solvation coordinate, $H \equiv h_b - h_a$. (25)

The system is assumed to be initially in the donor state, with $ρ(0) = |a⟩⟨a|ρ_{eq}^a$, where the bath Hamiltonian assumes $h_b = h_a$; i.e., $ρ_{eq}^a = ρ_{eq}^b ≈ e^{-βh_a}$. It also defines the solvation reorganization energy $\lambda = ⟨U⟩_b = tr_b(Uρ_{eq}^b)$ and the generalized Langevin force $F_b(t) = e^{iht_b}(U - λ)e^{-iht_a}$ that physically corresponds to the diffusive variable $Ω$ introduced in Sec. II B.

The reduced electron transfer system Hamiltonian reads now

$H = (E^o + λ)|b⟩⟨b| + V(|a⟩⟨b| + |b⟩⟨a|)$, (26)

while the dissipative system mode is

$Q = |b⟩⟨b|$. (27)

The following derivation of the analytical solutions to the transfer dynamics follows the same algebra as Ref. [30] where the HTA version was treated. By analyzing the tensor elements involved in Eq. (19b) for the specified dissipative mode $Q$ of Eq. (27), we find that the only nonzero tensor elements of $Π(n)$ remain to be

$x^{(n)} ≡ Π_{ba,ba}^{(n)}$, $y^{(n)} ≡ Π_{ba,ab}^{(n)}$, $z^{(n)} ≡ Π_{ba,bb}^{(n)}$, (28)

and their Hermitian conjugate counterparts. They are related to the Green’s function tensor elements, $X^{(n)} ≡ Π_{ba,ba}^{(n)}$, $Y^{(n)} ≡ Π_{ba,ab}^{(n)}$, $Z^{(n)} ≡ Π_{ba,bb}^{(n)}$, (29)

via [cf. Eq. (19b) and denoting $η ≡ cr − iε_i$]

$x^{(n)}(s) = η(n + 1)X^{(n+1)}(s + γ)$, $γ = (n + 1)Y^{(n+1)}(s + γ)$, $z^{(n)}(s) = (η − η^*)(n + 1)Z^{(n+1)}(s + γ)$. (30)

From Eq. (19a) and the associated Dyson equation method[36], we then obtain

$X^{(n)}(s) = [α^{(n)}(s) + β^{(n)}(s)]^/ζ^{(n)}(s)$, $Y^{(n)}(s) = [β^{(n)}(s) − y^{(n)}(s)]/ζ^{(n)}(s)$, $Z^{(n)}(s) = -\frac{1}{s}\{z^{(n)}(s) − iVX^{(n)}(s) + \{z^{(n)}(s) − iV^Y^{(n)}(s)\}$, (31)

with $ζ^{(n)}(s) ≡ |α^{(n)}(s) + β^{(n)}(s)|^2 - |β^{(n)}(s) − y^{(n)}(s)|^2$ and

$α^{(n)}(s) ≡ s + i(E^o + λ) + Δ + z^{(n)}(s)$, $β^{(n)}(s) ≡ sV[2V + iz^{(n)}(s)]$. (32)

The above formulations [Eqs. (28)–(32)] constitute the inverse recursive analytical evaluation of the required dissipation kernel $Π(s) ≡ Π^{(0)}(s)$, and also the Green’s function.

The forward and backward rate resolutions $k(s)$ and $k’(s)$ for the present two–level system of study can then be evaluated by using Eq. (24), resulting in

$k(s) = 2V^2Re \left\{ \frac{α(s) + y(s)}{|α(s)|^2 - |y(s)|^2} \right\}$, (33a)

and

$k’(s) = 2V^2Re \left\{ \frac{|α(s) + y(s)|[1 - iz^{*}(s)/V]}{|α(s)|^2 - |y(s)|^2} \right\}$. (33b)

The rate constants are the values at $s = 0$ for their steady state nature. The equilibrium reduced density matrix is obtained by solving $[i\mathcal{L} + Π(s = 0)]ρ^eq = 0$, together with $Tr[ρ^eq] = 1$. The solutions with $s = 0$ are

$ρ^eq_{bb} = 1 - ρ^eq_{aa} = \frac{Re(α + y)}{Re[(α + y)(2 - iz^*/V)]}$, (34a)

$ρ^eq_{ab} = ρ^eq_{ba} = -\frac{Re z}{Re[(α + y)(2 - iz^*/V)]}$. (34b)

Note that the electron transfer system considered here is different from the standard spin–boson model by their initial equilibrium bath states. The former is determined by $h_a = h_a$, while the latter by $h_a = \frac{1}{2}(h_a + h_b)$. This distinction results in different forms of the reduced system Hamiltonian and dissipative mode; thus different $ρ(t)$ dynamics. The steady–state behaviors would be the same, as required by thermodynamics principles, if the exact QDT is used. However, as here approximations are involved in treating the bath correlation function, the steady state behaviors such as rate constants and equilibrium system density matrix can be different in the aforementioned two model systems. Nevertheless, for either the standard electron transfer or spin–boson system, the algebra to analytical solutions is same.

IV. NUMERICAL VALIDATIONS

In this section we shall show that the proposed HQME is remarkably superior over the original HTA/ZE scheme. We address the issues of validity and applicability by considering the positivity and accuracy of the reduced density matrix dynamics. A versatile criterion for the range of applicability of the HQME will be constructed later; see the next section. Numerical results are all reported in unit of $k_B T = 1$. 
For the issue of positivity, we focus on the asymptotic regime, characterized by the so-called P-region in the electron transfer parameters space, where the rate constants, \( k = k(s = 0) \) and \( k' = k'(s = 0) \), and the equilibrium density matrix all satisfy the positivity requirement. The latter amounts to \( \rho_{a\beta}^{eq} \geq \rho_{ab}^{eq} \). With the aid of the analytic results presented in Eqs. (33) and (34), we explore thoroughly the P–regions in the temperature–scaled parameters space, where the rate constants \( \lambda, \gamma, E^0 \). The latter amounts to \( \rho_{a\beta}^{eq} \geq \rho_{ab}^{eq} \). With the aid of the analytic results presented in Eqs. (33) and (34), we explore thoroughly the P–regions in the temperature–scaled parameters space, where the rate constants \( \lambda, \gamma, E^0 \).

The resulting positivity diagrams of the ZE are reported in Fig. 1, identical for endothermicity \( E^0 \) and \(-E^0\). The P–region is indicated by the arrow(s) associated with each curve (or pair of curves of same color). In general, the P–region is larger for higher temperature, as expected. Also, the P–region itself does not vary when the transfer coupling strength \( \beta V \leq 0.1 \), but changes quite dramatically as \( \beta V \) increases. Observations for two specific systems, as depicted in Fig. 1(a) and its inset, are as follows. For a classical barrierless \( (E^0 + \lambda = 0) \) system, the P–region in \((\lambda, \gamma)\)–subspace quickly shrinks with \( \beta V > 0.1 \), and the ZE violates positivity completely for \( \beta V \geq 1.04 \). For a symmetric \( (E^0 = 0) \) system, the P–region does not change much, if \( \beta V \leq 1 \), covering over all \( \beta \lambda < 11 \); however, when \( 1 < \beta V < 4.5 \), it confines only within certain range of \( \beta \lambda \) depending on the value of \( \beta \gamma \). The ZE violates positivity completely for \( V > 4.5 \) for a

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**FIG. 1:** Positivity diagram of Zusman equation, where the P–region is indicated by the arrow or arrows associated with each curve or each pair of curves in same color. (a): Diagram in \((\lambda, \gamma; V)\)–subspace (with some selected values of \( V \)) for classical barrierless \((E^0 + \lambda = 0)\) and symmetric \((E^0 = 0; \text{ inset})\) systems, (b): Diagram in \((\lambda, \gamma; E^0)\)–subspace for \( V = 1 \) and 0.1 (inset). (c): Same as (b) but plotted in \((E^0, \lambda; \gamma)\)–subspace. Unit of \( k_B T = 1 \) is used.

**FIG. 2:** Population evolutions: Exact (black), HQME (red), and HTA/ZE (blue), for the specified systems. For the parameter \( \kappa \), see Eq. (35). Unit of \( k_B T = 1 \) is used.

**FIG. 3:** Same as Fig 2 but for systems with the common \((E^0, V, \lambda) = (-0.5, 1, 13)\), and different values of \( \gamma \), specified individually in each panel. Unit of \( k_B T = 1 \) is used.
symmetric system. Apparently, the applicability range of HTA/ZE scheme depends not just on bath interaction parameters, but also sensitively on system itself, leading to the complicated P-region diagrams, as depicted in Fig. 1.

The HQME is simply superb. While the ZE is subject to severe positivity violation especially for $\beta V > 1$, the new scheme is found to have P-region covering over a broad range of parameters space, as tested: $\beta\lambda < 25$, $\beta\gamma < 100$, $|\beta E^c| < 25$, and $\beta V < 100$. In other words, the HQME scheme preserves positivity, at least asymptotically, in almost entire parameters space of practical interest. Moreover, it is likely to support a convenient and system–insensitive criterion for its range of applicability; see the next section.

The HQME shows also its superiority in time evolution. It follows the exact results closer than the HTA/ZE does. Figure 2 depicts the transfer population evolutions of HQME, ZE, and exact HEOM. Chosen here are a classical barrierless system ($E^c + \lambda = 0$) in the main panel and a symmetric system ($E^c = 0$) in the inset. In contrast to the ZE that evolves into unphysical regime of positivity violation, the HQME remains accurate quantitatively and semi–quantitatively, respectively, for the two specified systems in study. Figure 3 is for three other systems, with common $\beta V$, $\beta\lambda$, and $\beta E^c$, but different values of $\beta\gamma$, where the intermediate one ($\beta\gamma = 5$) leads to the ZE dynamics violation of positivity. In all cases studied, the HQME performs much better than the HTA/ZE does. The superiority can be qualitative. While the HTA/ZE violates the positivity, the HQME can remain even quantitatively applicable.

V. DISCUSSION AND COMMENTS

A. Criterion and measure on applicability

For the issue of applicability, we propose to use

$$\kappa = \sqrt{6\Gamma(\gamma)/(\beta\lambda\gamma)},$$  \hspace{1cm} (35a)

with

$$\beta\Gamma(\gamma) = 6 + \sqrt{12 + (\beta\gamma)^2},$$  \hspace{1cm} (35b)

to estimate both the range of applicability (setting to be $\kappa > 1$) and the quality of HQME dynamics. The HQME dynamics tends to be more accurate for a larger $\kappa$ case. Justifications on the above criterion will be made in the next subsection.

We had indicated in Fig. 2 and Fig. 3 their associated values of the $\kappa$ parameter. The above system–independent criterion based on $\kappa$ is shown to be overall satisfactory. A quantitative agreement of HQME with the exact HEOM dynamics would depend on the specific details of systems. However, the system dependence is relatively insensitive, comparing to that on the nature of bath characterized by the parameter $\kappa$.

To further demonstrate this property of the HQME, we report in Figs. 4–6 the results of transfer dynamics for three pairs of systems that are chosen rather arbitrarily. Two systems in a pair share a common $(\lambda, \gamma)$, and thus, are associated with one value of $\kappa$, as indicated in each figure. These results all indicate that the proposed HQME supports a broad range of applicability, which can be fairly well described by the quality parameter $\kappa$ of Eq. (35).

All six cases presented in Figs. 4–6 are chosen to have the HTA/ZE unphysical, falling outside of its P–region, cf. Fig. 1. The corresponding HTA/ZE dynamics are therefore all wrong qualitatively and not shown. Rather we compare the results with an alternative HQME construction, labeled as M-HQME. This alternative is based on a similar approximation of the bath correlation function, but treated on the Matsubara series expansion of Eq. (A.1). The resulting M-HQME differs from the present HQME only by the values of parameters $c_r$ and $\Delta$. Instead of Eq. (9), the M-HQME assumes $c_r = Re c_0 = \lambda\gamma\cot(\frac{\beta\lambda\gamma}{2})$ and $\Delta = \Delta_0 = \lambda(\frac{\beta\gamma}{2} - \cot(\frac{\beta\gamma}{2}))$, from Eqs. (A.2) and (A.3), respectively. Apparently, the present HQME [Eq. (10) with Eq. (9)], not just removes the singularity of cotangent function, but also performs better in dynamics, as compared to the exact results.

FIG. 4: Population evolutions: Exact (black), HQME (red), and M-HQME (green), for $(E^c, V) = (-1, 0.5)$ (lower) and $(E^c, V) = (-5, 3.5)$ (upper), respectively, with same bath parameters of $(\lambda, \gamma) = (20, 5)$ that result in $\kappa = 0.85$. Both systems disqualify the HTA/ZE for its violating positivity. Unit of $k_B T = 1$ is used.
versus its high-temperature version, itatively distinct modifications, especially with spectively. However, the resulting HQME acquires qual-
approximation involved in each of them individually is
periority of HQME over HT A/ZE. Note that the only
involved in
therefore be addressed by examining the approximation
of transfer systems. The applicability of HQME may
in fact been verified extensively in our numerical study
criterion for its range of applicability. This argument has
fusion modified
sensitively on system.

B. Justification of the quality parameter

Let us start with some insights for the qualitative su-
periority of HQME over HT A/ZE. Note that the only
approximation involved in each of them individually is
the semiclassical bath correlation function \( C_{sc}(t) \) [Eq. (10)]
versus its high-temperature version, \( C_{HTA}(t) \) [Eq. (2)], re-
spectively. However, the resulting HQME acquires qual-
ifitatively distinct modifications, especially with \( i\mathcal{L}' = i\mathcal{L} + \delta \mathcal{R} \) appearing in Eq. (10), that lead to its being at least qualitatively consistent with the exact theory [Eq. (A.3)]. Physically, \( \delta \mathcal{R} \) serves as a diffusion correction to the effective system Liouvillian, due to the approximated treatment of bath correlation function. The HTA/ZE scheme, where \( \delta \mathcal{R} = 0 \), does not have this diffusion modification to the system Liouvillian. Consequently, the applicability range of HTA/ZE depends not just on bath correlation function \( C_{HTA}(t) \), but also sensitively on system.

The HQME dynamics that includes explicitly the dif-
fusion modified \( \mathcal{L}' \) may thus support a system-insensitive
criterion for its range of applicability. This argument has
in fact been verified extensively in our numerical study
of transfer systems. The applicability of HQME may therefore be addressed by examining the approximation involved in \( C_{sc}(t) \). We quantify the approximation with
the discrepancy function in the frequency-domain,
\[
\delta C(\omega) = C(\omega) - [C_{sc}(\omega) - \Delta] \\
= J(\omega) \left( \frac{1}{1 - e^{-\beta \omega}} - \frac{1}{\beta \omega} - \frac{1}{2} - \frac{\beta \omega}{12} \right) + \Delta \\
= \frac{\lambda \gamma \omega}{\omega^2 + \gamma^2} \left( \coth \frac{\beta \omega}{2} - \frac{2}{\beta \omega} + \frac{\beta \gamma^2}{6\omega} \right).
\]

The Drude model of Eq. (3) and \( \Delta = \beta \lambda \gamma / 6 \) are used explicitly in the last identity. The discrepancy function is positive, symmetric, and monotonic decreasing, with the limiting values of \( \delta C(\omega = 0) = \Delta \) and \( \delta C(\omega \to \infty) = 0 \). It is demonstrated in the inset of Fig. 7. Now let \( \Gamma(\gamma) \) be the half-width at half-maximum, determined via
\[
\delta C(\omega)|_{\omega = \Gamma(\gamma)} = \frac{\Delta}{2} = \frac{\beta \lambda \gamma}{12}.
\]

It can be well approximated by Eq. (35). The resulting
\( \Gamma(\gamma) / \gamma \), as participated in Eq. (35), is demonstrated in Fig. 7 with no visible difference from the numerically exact evaluation of Eq. (37).

The criterion on applicability of HQME can now be considered for the condition under which \( \delta C(\omega) \) can be treated as Markovian white noise for its effect of \( \delta \mathcal{R} \) on dissipative systems. We adopt the Kubo’s modulation parameter \( \kappa \) for the criterion: \( \kappa = \sqrt{\Gamma(\gamma) / \Delta} = \frac{\beta \lambda \gamma}{12} \).
\[ \sqrt{6\Gamma(\gamma)/\beta\gamma} > 1. \] This is the quality parameter of Eq. (35).

The range of applicability of HQME, as depicted by the region of \( \kappa > 1 \) in Fig. 8 is quite impressive. Consider, for example, the fact that it covers the value of \( \beta\gamma < 1 \), when \( \beta\gamma < 1 \). For a rather fast solvation of \( \gamma^{-1} = 100 \) fs, that \( \beta\gamma < 1 \) would support temperature \( T > 75 \) K and reorganization energy at least the range of \( \lambda < 3000 \) cm\(^{-1}\). This covers almost all systems of practical interest. Note that all dynamics results presented in this work are in the strong system–bath coupling regime. Let \( \alpha \) be the dimensionless system–bath coupling strength parameter, defined via \( J(\omega)/\omega|_{\omega=0} = \pi\alpha/2 \), as the Kondo parameter in the Ohmic model. We have \( \alpha = 4\lambda/(\pi\gamma) \). The present HQME would support \( \alpha < 72 \), with \( \gamma^{-1} = 100 \) fs and \( T = 75 \) K, if \( \kappa > 1 \) criterion is used. The calculations demonstrated in this paper have the coupling strength ranging from \( \alpha = 0.95 \) (Fig. 2 and Fig. 3) to \( \alpha = 33 \) (the lower panel of Fig. 3).

VI. CONCLUDING REMARKS

We have proposed the HQME that may be used with good confidence to arbitrary systems. The theoretical development is rooted in an improved semiclassical treatment of Drude bath. This alone improves the conventional high–temperature or classical approximation by two or three orders in temperature parameter, respectively, as argued in Sec. I. The resulting HQME can be considered as a natural extension and modification of the conventional stochastic Liouville equation and Zusman equation. While it retains their appealing physical pictures and numerical efficiency, the HQME shows remarkable improvement over the conventional theories. Its broad range of validity and applicability, in terms of density matrix positivity and dynamics quality, are extensively demonstrated on two–level model systems. We have also proposed a criterion to estimate the performance of HQME. This criterion depends only on the system–bath coupling strength, characteristic bath memory time and temperature. Our results all reveal that the HQME may serve as a versatile tool wherever the exact approach is numerically too expensive to afford.

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APPENDIX: EXACT HEOM FORMALISM

The HEOM formalism for the reduced system dynamics can be constructed using the calculus–on–path–integral technique.\(^{5,6,7,8,9,10,11,12,13}\) This formalism is in principle exact and nonperturbative. However, its specified form depends on the way of treating the bath correlation function, under the constraint of the exact fluctuation–dissipation theorem [Eq. (3)]. Consider the Matsubara expansion method, in which the bath correlation function with the Drude model of Eq. (3) reads

\[ C(t > 0) = c_0 e^{-\gamma t} + \sum_{k=1}^{\infty} c_k e^{-\gamma_k t}. \] (A.1)

The first term, with

\[ c_0 = \lambda \gamma \left[ \cot (\gamma/2) - i \right], \] (A.2)
arises from the Drude pole. The sum term arises from the Matsubara poles or frequencies of \( \gamma_{k \geq 1} = 2k\pi/\beta \), with

\[
c_k = \frac{8k\pi\lambda\gamma}{(2k\pi)^2 - (\beta\gamma)^2}; \quad k \geq 1. \tag{A.3}
\]

To construct the HEOM, the infinite sum over the \( k \) index in Eq. (A.1) need to be truncated. To that end, let \( \gamma_0 \equiv \gamma \) and recast Eq. (A.1) by

\[
C(t) = \sum_{k=0}^{K} c_k e^{-\gamma_k t} + 2\Delta_K \delta(t), \tag{A.4}
\]

where

\[
\Delta_K \equiv \sum_{k=K+1}^{\infty} \frac{c_k}{\gamma_k} = \lambda \left[ \frac{2}{\beta\gamma} - \cot\left(\frac{\beta\gamma}{2}\right) \right] - \sum_{k=1}^{K} \frac{c_k}{\gamma_k}. \tag{A.5}
\]

This treatment is in principle exact if the \( K \) is chosen large enough and the resulting reduced system density matrix dynamics of primary interest is converged.

The resulting HEOM formalism reads

\[
\dot{\rho}_n = -\left( i\mathcal{L} + \delta\mathcal{R}_K + \sum_{k=0}^{K} n_k \gamma_k \right) \rho_n
- i \sum_{k=0}^{K} \sqrt{(n_k + 1)|c_k|} [Q, \rho_{n_k}^+]
- i \sum_{k=0}^{K} \sqrt{n_k/|c_k|} \left( c_k Q \rho_{n_k^-} - c_k^* \rho_{n_k}^- Q \right), \tag{A.6}
\]

with

\[
\delta\mathcal{R}_K \hat{O} = \Delta_K [Q, [Q, \hat{O}]]. \tag{A.7}
\]

The reduced density operator of primary interest is \( \rho \equiv \rho_0 \). The subscript \( n = \{ n_k \geq 0; \; k = 0, \ldots, K \} \), which consists of a set of nonnegative indices, specifies in general a given auxiliary density operator (ADO) of \( \rho_n \equiv \rho_{n_0\cdots n_K} \). The subscript \( n_k \) differs from \( n \) only by changing the specified \( n_k \) to \( n_k \pm 1 \). An \( N^{th} \)-tier ADO is of \( n_0 + \cdots + n_K = N \), and the total number of ADOs at this tier is \( (N+K)! \). Each \( \rho_n \) in Eq. (A.6) has been scaled individually to have a uniform dimension and error tolerance. This validates a simple, on–the–fly , filtering algorithm for efficient numerical propagation, including automatic truncation of hierarchy. However, the exact HEOM calculations is still numerically expensive, especially for complex systems, under strong coupling with bath at low temperature.
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1 R. P. Feynman and F. L. Vernon, Jr., Ann. Phys. 24, 118 (1963).
2 U. Weiss, Quantum Dissipative Systems, World Scientific, Singapore, 2008, 3rd ed. Series in Modern Condensed Matter Physics, Vol. 13.
3 H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, World Scientific, Singapore, 2009, 5th ed.
4 Y. Tanimura, J. Phys. Soc. Jpn. 75, 082001 (2006).
5 Y. Tanimura and R. Kubo, J. Phys. Soc. Jpn. 58, 101 (1989).
6 Y. Tanimura, Phys. Rev. A 41, 6676 (1990).
7 Y. Tanimura and P. G. Wolynes, Phys. Rev. A 43, 4131 (1991).
8 Y. Tanimura and S. Mukamel, J. Phys. Soc. Jpn. 63, 66 (1994).
9 A. Ishizaki and Y. Tanimura, J. Phys. Soc. Jpn. 74, 3131 (2005).
10 R. X. Xu, P. Cui, X. Q. Li, Y. Mo, and Y. J. Yan, J. Chem. Phys. 122, 041103 (2005).
11 R. X. Xu and Y. J. Yan, Phys. Rev. E 75, 031107 (2007).
12 J. S. Jin, X. Zheng, and Y. J. Yan, J. Chem. Phys. 128, 234703 (2008).
13 X. Zheng, J. S. Jin, S. Welack, M. Luo, and Y. J. Yan, J. Chem. Phys. 130, 164708 (2009).
14 Q. Shi, L. P. Chen, G. J. Nan, R. X. Xu, and Y. J. Yan, J. Chem. Phys. 130, 084105 (2009).
15 Q. Shi, L. P. Chen, G. J. Nan, R. X. Xu, and Y. J. Yan, J. Chem. Phys. 130, 164518 (2009).
16 Y. A. Yan, F. Yang, Y. Liu, and J. S. Shao, Chem. Phys. Lett. 395, 216 (2004).
17 Y. Zhou and J. S. Shao, J. Chem. Phys. 128, 034106 (2008).
18 R. Kubo, J. Math. Phys. 4, 174 (1963).
19 R. Kubo, Adv. Chem. Phys. 15, 101 (1969).
20 D. Abramavicius, B. Palmieri, D. V. Voronine, F. Šanda, and S. Mukamel, Chem. Rev. 109, 2350 (2009).
21 W. Zhuang, T. Hayashi, and S. Mukamel, Angew. Chem. Int. Ed. 48, 3750 (2009).
22 L. D. Zusman, Chem. Phys. 49, 295 (1980).
23 L. D. Zusman, Chem. Phys. 80, 29 (1983).
24 A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. 83, 4491 (1985).
25 D. Y. Yang and R. I. Cukier, J. Chem. Phys. 91, 281 (1989).
26 P. A. Frantsuzov, Chem. Phys. Lett. 267, 427 (1997).
27 P. A. Frantsuzov, J. Chem. Phys. 111, 2075 (1999).
28 M. Thoss, H. B. Wang, and W. H. Miller, J. Chem. Phys. 115, 2991 (2001).
29 Y. J. Jung and J. S. Cao, J. Chem. Phys. 117, 3822 (2002).
30 L. Mühlbacher and R. Egger, J. Chem. Phys. 118, 179 (2003).
31 J. Ankerhold and H. Lehle, J. Chem. Phys. 120, 1436 (2004).
32 D. V. Dodin, Chem. Phys. 325, 257 (2006).
33 M.-L. Zhang, S.-S. Zhang, and E. Pollak, J. Chem. Phys. 119, 11864 (2003).
34 M.-L. Zhang, S.-S. Zhang, and E. Pollak, J. Chem. Phys. 120, 9630 (2004).
35 R. Kubo, M. Toda, and N. Hashitsume, Statistical Physics II: Non-equilibrium Statistical Mechanics, Springer-Verlag, Berlin, 2nd Ed., 1985.
36 P. Han et al., J. Phys. Chem. B 110, 11438 (2006).