Fokker–Planck quantum master equation for mixed quantum–semiclassical dynamics

Jin-Jin Ding,[1,2,a)] Yao Wang,[2,a)] Hou-Dao Zhang,[2,b)] Rui-Xue Xu,[2] Xiao Zheng,[2] and YiJing Yan[2,c)]

[1]*School of Chemistry and Chemical Engineering, Nantong University, Nantong, Jiangsu 226019, China*
[2]*Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemical Physics and iChEM and Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*

We revisit Caldeira–Leggett's quantum master equation representing mixed quantum–classical theory, but with limited applications. Proposed is a Fokker–Planck quantum master equation theory, with a generic bi–exponential correlation function description on semiclassical Brownian oscillators' environments. The new theory has caustic terms that bridge between the quantum description on primary systems and the semiclassical or quasi–classical description on environments. Various parametrization schemes, both analytical and numerical, for the generic bi–exponential environment bath correlation functions are proposed and scrutinized. The Fokker–Planck quantum master equation theory is of the same numerical cost as the original Caldeira–Leggett's approach but acquires a significantly broadened validity and accuracy range, as illustrated against the exact dynamics on model systems in quantum Brownian oscillators' environments, at moderately low temperatures. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4973610]

I. INTRODUCTION

Correlated system–and–bath coherence is a type of quantum entanglement and occurs whenever the quantum nature of environment cannot be neglected. It plays ever increasing important roles in many fields of science. Traditionally this problem is addressed via the hybrid quantum master equation (QME) approach.[1–6] This is to divide the overall environment into the "first–shell" and "secondary" parts. The latter assumes Markovian for its influence on the first–shell (solvation hereafter) dynamics. The most representing theory of this kind may be Caldeira–Leggett's QME,[6] in which both the primary system and solvation mode(s) are treated explicitly. However, Caldeira–Leggett's approach involves the classical Brownian oscillator motion treatment on environments. This significantly compromises the range of applicability, as the underlying solvation dynamics is *purely* classical, without quantum system influence. The same problem occurs also in many mixed quantum–classical master equation methods.[4–9] Caustic corrections are needed to bridge between the quantum description on systems and the classical description on environments.[10]

In this work, we develop a unified Fokker–Planck quantum master equations (FP-QMEs) theory, with the *semiclassical* Brownian oscillators environments assuming a generic bi-exponential correlation function form. Exploited in the derivations is the hierarchical–equations–of–motion (HEOM) formalism,[11–16] an alternative approach to correlated

system–and–bath coherence. Its relation to the diffusion limit of Caldeira–Leggett's QME, the Zusman equation,[4,5] had been established.[17] This leads further to a modified semiclassical Zusman equation, with a significantly improved range of applicability and convenient accuracy control, at no extra numerical cost.[18,19]

The present work extends the aforementioned method to the construction of a unified FP-QMEs theory. The resulting FP-QMEs contain caustic terms that are missing in the original Caldeira–Leggett's mixed quantum–classical theory.[6] These terms arise naturally by considering both the short–time and long–time properties of bath correlation functions. These caustic terms properly bridge between the quantum and semiclassical descriptions. The correlations, at either quasi–classical or semiclassical level, are rather simple and appealing, with solid grounds and remarkable improvements. It is anticipated that the present work will benefit the advancement of semiclassical methods for complex systems in general, where exact results are unobtainable.

This paper is organized as follows. In Sec. II, we present the backgrounds on the hybrid system–and–bath description and Caldeira–Leggett's QME. After presenting the FP operator algebra in Appendix A, we derive in detail a unified FP–QMEs theory, for the semiclassical Brownian oscillators environment with generic bi–exponential bath correlation functions, in Appendix B. In Sec. III, we summarize the unified FP–QMEs theory, and highlight its HEOM equivalence. FP–QMEs are all of the same numerical cost as the original Caldeira–Leggett's approach, due to the underlying HEOM dynamics, with the generic bi–exponential bath environment couplings. Among several analytical parametrization schemes considered in Sec. IV, we identity the best one, and validate the

a)J.-J. Ding and Y. Wang contributed equally to this work.
b)Electronic address: hdz@ustc.edu.cn
c)Electronic address: yanyj@ustc.edu.cn

resulting optimal FP–QME with a broad range of applicability. The least–square–fit results are also presented and compared with those of the best analytical scheme considered in this work. We conclude this work in Sec. V.

II. PRELUDE

A. Characterization of Gaussian bath influence

Consider the total system–and–bath composite Hamiltonian,

$$H_{\mathrm{T}} = H_{\mathrm{S}} + \hat{Q}_{\mathrm{S}} \sum_k c_k x_k + \frac{1}{2} \sum_k \omega_k (p_k^2 + x_k^2)$$
$$\equiv H_{\mathrm{S}} + \hat{Q}_{\mathrm{S}} \hat{x}_{\mathrm{B}} + h_{\mathrm{B}}. \quad (1)$$

The system Hamiltonian H_{S} and dissipation mode $\hat{Q}_{\mathrm{S}}$ are arbitrary. The bath h_{B} defined above assumes a collection of noninteracting oscillators. Throughout this paper, we set $\hbar = 1$ and $\beta = 1/(k_B T)$, with k_B and T being the Boltzmann constant and temperature, respectively. Denote $\langle \hat{O} \rangle_{\mathrm{B}} \equiv \mathrm{tr}_{\mathrm{B}}(\hat{O} e^{-\beta h_{\mathrm{B}}})/\mathrm{tr}_{\mathrm{B}} e^{-\beta h_{\mathrm{B}}}$, for an average over the bare bath ensemble.

Defined in Eq. (1) is also $\hat{x}_{\mathrm{B}} = \sum_k c_k x_k$, which is set to be dimensionless. This is a macroscopic solvation bath coordinate that hybridizes with the system. Denote the causality transformation on the solvation bath response function,[20,21]

$$\chi_{\mathrm{B}}(\omega) \equiv i \int_0^\infty \mathrm{d}t\, e^{i\omega t} \langle [\hat{x}_{\mathrm{B}}(t), \hat{x}_{\mathrm{B}}(0)] \rangle_{\mathrm{B}}. \quad (2)$$

The solvation bath correlation function can be evaluated via the fluctuation–dissipation theorem,[20,21]

$$\langle \hat{x}_{\mathrm{B}}(t) \hat{x}_{\mathrm{B}}(0) \rangle_{\mathrm{B}} = \frac{1}{\pi} \int_{-\infty}^\infty \mathrm{d}\omega\, e^{-i\omega t} \frac{\chi_{\mathrm{B}}''(\omega)}{1 - e^{-\beta\omega}}, \quad (3)$$

with

$$\chi_{\mathrm{B}}''(\omega) \equiv \mathrm{Im}\chi_{\mathrm{B}}(\omega) \equiv J(\omega). \quad (4)$$

This defines the solvation spectral density, which completely characterizes the Gaussian bath influence.[20–22] Equation (3) with $t > 0$ denotes the forward (retarded) solvation bath correlation function. The time–reversal counterpart follows[20,21]

$$\langle \hat{x}_{\mathrm{B}}(0) \hat{x}_{\mathrm{B}}(t) \rangle_{\mathrm{B}} = \langle \hat{x}_{\mathrm{B}}(t) \hat{x}_{\mathrm{B}}(0) \rangle_{\mathrm{B}}^*. \quad (5)$$

The causality transformation on the solvation bath correlation function is[20,21]

$$\hat{C}(\omega) \equiv \int_0^\infty \mathrm{d}t\, e^{i\omega t} \langle \hat{x}_{\mathrm{B}}(t) \hat{x}_{\mathrm{B}}(0) \rangle_{\mathrm{B}} \equiv C(\omega) + iD(\omega), \quad (6)$$

with its real and imaginary parts being the spectrum and dispersion, respectively. The spectrum is given by the Fourier integrand in Eq. (3); i.e. [cf. Eq. (4)],

$$C(\omega) = \frac{J(\omega)}{1 - e^{-\beta\omega}}. \quad (7)$$

Dispersion is related to the spectrum via the Kramers-Kronig relation[20,21]

$$D(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^\infty \mathrm{d}\omega' \frac{C(\omega')}{\omega - \omega'}. \quad (8)$$

Here, $\mathcal{P}$ denotes the principle part. An important result of the above relations is

$$\hat{C}(\omega = 0) = \frac{J(\omega)}{1 - e^{-\beta\omega}}\Big|_{\omega=0} - \frac{i}{2\pi} \int_{-\infty}^\infty \mathrm{d}\omega \frac{J(\omega)}{\omega}. \quad (9)$$

This will be used later, together with the Brownian oscillator bath model considered in this work,

$$J(\omega) = \frac{\Omega\zeta\omega}{(\Omega^2 - \omega^2)^2 + \zeta^2\omega^2}. \quad (10)$$

Both the frequency Ω and friction constant ζ are positive, and related to the exponents,

$$\gamma_{1(2)} = \frac{1}{2}\left[\zeta \pm (\zeta^2 - 4\Omega^2)^{\frac{1}{2}}\right]. \quad (11)$$

Equation (3) in the Matsubara expansion form reads[20,21]

$$\langle \hat{x}_{\mathrm{B}}(t) \hat{x}_{\mathrm{B}}(0) \rangle_{\mathrm{B}} = \eta_1 e^{-\gamma_1 t} + \eta_2 e^{-\gamma_2 t} + \sum_{m=1}^\infty \breve{\eta}_m e^{-\breve{\gamma}_m t}. \quad (12)$$

Here, $\{\breve{\gamma}_m = 2\pi m/\beta; m = 1, 2, ...\}$ are the Matsubara frequencies. The pre–exponential coefficients are the residues of the Cauchy's contour integration in the lower–half plane. In this work, instead of the above exact but infinity series expansion, we will focus on a semiclassical description of environments, with the solvation bath correlation function in a bi–exponential approximant form.

B. The hybrid system–and–bath description

We turn to the hybrid description, in which the overall bath, $h_{\mathrm{B}} = \frac{1}{2} \sum_k \omega_k (p_k^2 + x_k^2)$ in Eq. (1), is divided into the solvation mode and secondary bath parts, that is,[6,23]

$$h_{\mathrm{B}} = \frac{1}{2}\Omega\left(\hat{p}_{\mathrm{B}}^2 + \hat{x}_{\mathrm{B}}^2\right) + \frac{1}{2}\sum_j \tilde{\omega}_j\left[\tilde{p}_j^2 + \left(\tilde{x}_j - \frac{\tilde{c}_j}{\tilde{\omega}_j}\hat{x}_{\mathrm{B}}\right)^2\right]. \quad (13)$$

The solvation mode of frequency Ω, with coordinate $\hat{x}_{\mathrm{B}}$ and momentum $\hat{p}_{\mathrm{B}}$, is a Brownian oscillator, subject to the stochastic force, $\tilde{F}(t) = e^{i\tilde{h}_{\mathrm{B}}t}\left(\sum_j \tilde{c}_j \tilde{x}_j\right)e^{-i\tilde{h}_{\mathrm{B}}t}$, by the secondary $\{\tilde{h}_{\mathrm{B}}\}$–bath environment. The resulting Langevin equation reads[20,21]

$$\dot{\hat{p}}_{\mathrm{B}}(t) = -\Omega\hat{x}_{\mathrm{B}} - \int_0^t \mathrm{d}\tau\, \tilde{\zeta}(t - \tau)\hat{p}_{\mathrm{B}}(\tau) + \tilde{F}(t), \quad (14)$$

where $\tilde{\zeta}(t) = \Omega \sum_j (\tilde{c}_j^2/\tilde{\omega}_j) \cos(\tilde{\omega}_j t)$, the classical friction function. It is easy to obtain with Eq. (2) the expression[20,21]

$$\chi_{\mathrm{B}}(\omega) = \frac{\Omega}{\Omega^2 - \omega^2 - i\omega\zeta(\omega)}, \quad (15)$$

where

$$\zeta(\omega) \equiv \int_0^\infty \mathrm{d}t\, e^{i\omega t} \tilde{\zeta}(t). \quad (16)$$

The secondary bath spectral density is then[2,20]

$$\tilde{J}(\omega) = \frac{\omega}{\Omega}\mathrm{Re}\,\zeta(\omega) = \frac{\chi_{\mathrm{B}}''(\omega)}{|\chi_{\mathrm{B}}(\omega)|^2}. \quad (17)$$

C. Caldeira–Leggett's QME with classical bath

The bath spectral density $J(\omega)$ of Eq. (10) used in this work assumes the secondary bath to be Markovian. This is $\tilde{\zeta}(t - \tau) \approx 2\zeta\delta(t - \tau)$ in Eq. (14), leading to Eq. (16) $\zeta(\omega) \approx \zeta = \zeta(\omega = 0)$. Together with Eqs. (15) and (4), we obtain Eq. (10), and via Eq. (17) further that $\tilde{J}(\omega) = \zeta\omega/\Omega$.

However, the secondary bath spectrum, $\tilde{C}(\omega) \equiv \tilde{J}(\omega)/(1 - e^{-\beta\omega})$ [cf. Eq. (7)], is in general not a white noise, unless the high–temperature approximation,

$$\frac{1}{1 - e^{-\beta\omega}} \approx \frac{1}{2} + \frac{1}{\beta\omega}, \qquad (18)$$

is also adopted. In this case, $\tilde{C}(\omega) \approx \zeta/(\beta\Omega) + \zeta\omega/(2\Omega)$. The corresponding secondary bath correlation function is a white noise, $\tilde{C}(t) \approx [2\zeta/(\beta\Omega)]\delta(t) + i(\zeta/\Omega)\dot\delta(t)$. One can then obtain Caldeira–Leggett's QME,[6,20,24,25]

$$\dot{\rho}^{\mathrm{HT}}(t) = -i[H_S + \hat{Q}_S \hat{x}_B, \rho^{\mathrm{HT}}(t)] - \mathcal{L}_{\mathrm{FP}}^{\mathrm{HT}} \hat{\rho}^{\mathrm{HT}}(t), \qquad (19)$$

with the classical FP operator,[26]

$$\mathcal{L}_{\mathrm{FP}}^{\mathrm{HT}} \hat{\rho} = i\frac{\Omega}{2}[\hat{p}_B^2 + \hat{x}_B^2, \hat{\rho}] + \frac{\zeta}{\beta\Omega}[\hat{x}_B, [\hat{x}_B, \hat{\rho}]]$$
$$+ i\frac{\zeta}{2}[\hat{x}_B, \{\hat{p}_B, \hat{\rho}\}]. \qquad (20)$$

As a classical bath theory, Caldeira–Leggett's QME is of a rather limited applicability range in the parameter space. In this mixed quantum–classical description, the incoherence is completely described by the last two terms in the classical FP operator, $\mathcal{L}_{\mathrm{FP}}^{\mathrm{HT}}$ of Eq. (20), containing no system variables at all. Modifications are needed, with caustic dephasing contributions that depend on both bath and system.

In contact with the later development, let us examine the high–temperature approximation, directly on the solvation correlation function, Eq. (3), for the BO bath of Eq. (10), assuming $\zeta/2 \neq \Omega$. We have

$$\langle \hat{x}_B(t)\hat{x}_B(0)\rangle_B^{\mathrm{HT}} \approx \eta_1^{\mathrm{HT}} e^{-\gamma_1 t} + \eta_2^{\mathrm{HT}} e^{-\gamma_2 t}, \qquad (21)$$

with the exponents of Eq. (11), and

$$\eta_1^{\mathrm{HT}} = -\frac{\Omega}{\gamma_1 - \gamma_2}\left(\frac{1}{\beta\gamma_1} - \frac{i}{2}\right),$$
$$\eta_2^{\mathrm{HT}} = \frac{\Omega}{\gamma_1 - \gamma_2}\left(\frac{1}{\beta\gamma_2} - \frac{i}{2}\right) \qquad (22)$$

The involving high–temperature coefficients satisfy

$$\eta_1^{\mathrm{HT}} + \eta_2^{\mathrm{HT}} = \langle \hat{x}_B^2 \rangle_B^{\mathrm{HT}} = \frac{1}{\beta\Omega}, \qquad (23a)$$

$$\eta_1^{\mathrm{HT}}\gamma_1 + \eta_2^{\mathrm{HT}}\gamma_2 = \frac{i\Omega}{2}. \qquad (23b)$$

The first expression is the value of Eq. (21) at $t = 0$. The second one, which is the negative to the time derivative of Eq. (21) at $t = 0$, happens to be the exact value of $-\langle \dot{\hat{x}}_B \hat{x}_B \rangle_B = \langle \hat{x}_B \dot{\hat{x}}_B \rangle_B = \Omega\langle \hat{x}_B \hat{p}_B \rangle_B = i\Omega/2$.

III. FOKKER–PLANCK QUANTUM MASTER EQUATION THEORY

A. The FP–QME with a semiclassical BO bath

We are interested in a modified theory, in the form of FP–QMEs, with the semiclassical BO environment, characterized by a generic bi-exponential approximation to Eq. (3) or Eq. (12),

$$\langle \hat{x}_B(t)\hat{x}_B(0)\rangle_B \approx \eta_+ e^{-\gamma_+ t} + \eta_- e^{-\gamma_- t}. \qquad (24)$$

The exponents are dictated by the effective BO frequency ($\bar{\Omega} > 0$) and friction ($\bar{\zeta} > 0$) parameters [cf. Eq. (11)],

$$\gamma_\pm \equiv \frac{1}{2}[\bar{\zeta} \pm (\bar{\zeta}^2 - 4\bar{\Omega}^2)^{\frac{1}{2}}]. \qquad (25)$$

The effective temperature–dependent BO frequency $\bar{\Omega}$ and friction $\bar{\zeta}$ could differ from the original Ω and ζ, especially at the low–temperature regime. While $\bar{\Omega}$ and $\bar{\zeta}$ are positive, η_+ and η_- in Eq. (24) are complex. All these parameters are to be identified, with some representing parametrization schemes, both quasi–classical and semiclassical, specified in Secs. IV A and IV B, respectively.

The proposed FP–QME theory, in relation to Eqs. (24) and (25), goes with the semiclassical FP operator [cf. Eq. (20)],

$$\mathcal{L}_{\mathrm{FP}}\hat{\rho} = i\frac{\bar{\Omega}}{2}[\hat{p}_B^2 + \hat{x}_B^2, \hat{\rho}] + \frac{\bar{\zeta}}{\beta\bar{\Omega}}[\hat{x}_B, [\hat{x}_B, \hat{\rho}]]$$
$$+ i\frac{\bar{\zeta}}{2}[\hat{x}_B, \{\hat{p}_B, \hat{\rho}\}]. \qquad (26)$$

We exploit the HEOM formalism[11–14,27] to derive the unified FP–QMEs theory, with the above generic bi–exponential ansatz on the bath correlation function. The final results read

$$\dot{\rho}(t) = -i[H_S + \hat{Q}_S \hat{x}_B, \hat{\rho}(t)] - \mathcal{L}_{\mathrm{FP}}\hat{\rho}(t) - \delta_0[\hat{Q}_S, [\hat{p}_B, \hat{\rho}(t)]]$$
$$- \delta_1[\hat{Q}_S, [\hat{x}_B, \hat{\rho}(t)]] - \frac{i\delta_2}{2}\{\hat{Q}_S, [\hat{x}_B, \hat{\rho}(t)]\}, \qquad (27)$$

with the three real parameters, δ_0, δ_1, and δ_2, satisfying

$$\eta_+ + \eta_- \equiv \frac{1}{\beta\bar{\Omega}} + \delta_0 \qquad (28a)$$

$$\eta_+\gamma_+ + \eta_-\gamma_- \equiv \bar{\Omega}\left[\delta_1 + \frac{i}{2}(1 + \delta_2)\right]. \qquad (28b)$$

Apparently, $\delta_0^{\mathrm{HT}} = \delta_1^{\mathrm{HT}} = \delta_2^{\mathrm{HT}} = 0$, as inferred from the high–temperature scheme of Eq. (23). Apparently, the last three terms in Eq. (27) are incoherent and also of the dependence on both system and bath. The physical pictures and implications of these caustic terms will be clarified in due course.

The derivations will go with the solvation–subspace Wigner representation, in which Eq. (27) reads

$$\frac{\partial}{\partial t}\rho_W = -(i\mathcal{L}_S + \hat{L}_{\mathrm{FP}})\rho_W$$
$$- i\left[\hat{Q}_S, x_B \rho_W\right] + \frac{1}{2}(1 + \delta_2)\left\{\hat{Q}_S, \frac{\partial}{\partial p_B}\rho_W\right\}$$
$$+ i\delta_0\left[\hat{Q}_S, \frac{\partial}{\partial x_B}\rho_W\right] - i\delta_1\left[\hat{Q}_S, \frac{\partial}{\partial p_B}\rho_W\right] \qquad (29)$$

with $\hat{L}_{\mathrm{FP}}$, the Wigner representation of $\mathcal{L}_{\mathrm{FP}}$ of Eq. (26), the expression of

$$\hat{L}_{\mathrm{FP}} = \bar{\Omega}\left(\frac{\partial}{\partial x_B}p_B - \frac{\partial}{\partial p_B}x_B\right) - \frac{\bar{\zeta}}{\beta\bar{\Omega}}\frac{\partial^2}{\partial p_B^2} - \bar{\zeta}\frac{\partial}{\partial p_B}p_B. \qquad (30)$$

This operator is non–Hermitian, which under the similarity transformation[26]

$$\tilde{L}_{\mathrm{FP}} \equiv e^S \hat{L}_{\mathrm{FP}} e^{-S}, \quad \text{with } S = \frac{1}{4}\beta\bar{\Omega}(x_B^2 + p_B^2), \qquad (31)$$

can be "diagonalized" as

$$\tilde{L}_{\mathrm{FP}}\Psi_{n_1 n_2}(x_B, p_B) = (n_1\gamma_+ + n_2\gamma_-)\Psi_{n_1 n_2}(x_B, p_B). \qquad (32)$$

See Appendix A for the detailed derivations and also the eigenfunctions $\{\Psi_{n_1 n_2}(x_B, p_B); n_1, n_2 = 0, 1, ...\}$.

B. Formal constructions and dynamical resolutions

Besides the properties of $\{\Psi_{n_1 n_2}(x_B, p_B)\}$, the derivations to FP–QME (29), which are detailed in Appendix B, exploit also the HEOM formalism[11–14,27]

$$
\begin{aligned}
\dot{\rho}_{n_1 n_2} = & -(i\mathcal{L}_S + n_1\gamma_+ + n_2\gamma_-)\rho_{n_1 n_2} \\
& - i\left[\hat{Q}_S, \rho_{n_1+1,n_2} + \rho_{n_1,n_2+1}\right] \\
& - in_1\left(\eta_+\hat{Q}_S\rho_{n_1-1,n_2} - \bar{\eta}_+^*\rho_{n_1-1,n_2}\hat{Q}_S\right) \\
& - in_2\left(\eta_-\hat{Q}_S\rho_{n_1,n_2-1} - \bar{\eta}_-^*\rho_{n_1,n_2-1}\hat{Q}_S\right).
\end{aligned} \tag{33}
$$

This is exact for the bi–exponential bath correlation function, Eq. (24). Note that $\gamma_\pm > 0$ when $\bar{\zeta}/2 > \bar{\Omega}$; and $\gamma_+ = \gamma_-^*$ when $\bar{\zeta}/2 < \bar{\Omega}$. The situation of $\bar{\zeta}/2 = \bar{\Omega}$ is not considered here. Adopted in Eq. (33) is also the notation[27]

$$
\bar{\eta}_\pm = \begin{cases} \eta_\pm, & \text{if } \gamma_\pm \text{ is real} \\ \eta_\mp, & \text{if } \gamma_+ = \gamma_-^* \end{cases}. \tag{34}
$$

The key relation that bridges the HEOM (33) and the FP–QME (29) is

$$
\begin{aligned}
\rho_W(p_B, x_B, t) = & \sum_{n_1, n_2} \frac{s_{n_1 n_2}}{\sqrt{n_1! \, n_2!}} \rho_{n_1 n_2}(t) \\
& \times e^{-\frac{1}{4}\beta\bar{\Omega}(x_B^2 + p_B^2)} \Psi_{n_1 n_2}(x_B, p_B),
\end{aligned} \tag{35}
$$

with

$$
s_{n_1 n_2} = (-1)^{n_1} \frac{\left(\sqrt{\beta\bar{\Omega}}\right)^{n_1 + n_2}}{r_2^{n_1} r_1^{n_2}}, \tag{36}
$$

where $r_1 = \sqrt{\gamma_+/(\gamma_+ - \gamma_-)}$ and $r_2 = \sqrt{\gamma_-/(\gamma_+ - \gamma_-)}$ [cf. Eq. (A4)].

As detailed in Appendix B, the FP–QME (29) can now be constructed via Eqs. (33)–(36), together with the basic results of Appendix A on the $\tilde{L}_{FP}$–eigenfunctions, $\{\Psi_{n_1 n_2}(x_B, p_B)\}$ of Eq. (32). Note that the individual HEOM's dynamical variable, $\rho_{n_1 n_2}(t)$, had been physically identified in the quasi–particle picture as a specified dissipatons–configuration.[28,29] Equation (35) offers now an alternative expression,

$$
\begin{aligned}
\rho_{n_1 n_2}(t) = & \frac{\sqrt{n_1! n_2!}}{s_{n_1 n_2}} \int\int dx_B dp_B \bar{\Psi}_{n_1 n_2}^*(x_B, p_B) \\
& \times e^{\frac{1}{4}\beta\bar{\Omega}(x_B^2 + p_B^2)} \rho_W(x_B, p_B, t).
\end{aligned} \tag{37}
$$

It involves the left–eigenfunctions $\{\bar{\Psi}_{n_1 n_2}\}$ for $\tilde{L}_{FP}$, as given by Eq. (A17) with Eq. (A18), by which $\langle\bar{\Psi}_{n_1 n_2}|\Psi_{n_1' n_2'}\rangle = \delta_{n_1 n_1'}\delta_{n_2 n_2'}$ [cf. Eq. (A13)]. The equivalence between the FP–QME (27) and the HEOM (33) is now completely established. The underlying entanglement evolution could then be addressed.

IV. QUASI–CLASSICAL VERSUS SEMICLASSICAL ENVIRONMENTS

A. Quasi–classical environment descriptors

To complete the FP–QME theory, we shall properly determine the bi-exponential parameters for the semiclassical solvation correlation function of Eq. (24). The general case of temperature–dependent exponents will be considered in Sec. IV B.

To clarify the physical pictures of the caustic terms in Eq. (27), this subsection focuses on the simplified scenario, in which $\gamma_\pm = \gamma_{1(2)}$ of Eq. (11). This is a quasi–classical bath setup, assuming [cf. Eq. (24)]

$$
\langle \hat{x}_B(t)\hat{x}_B(0)\rangle_B \approx \eta_+ e^{-\gamma_1 t} + \eta_- e^{-\gamma_2 t}. \tag{38}
$$

Only the coefficients η_+ and η_- are to be determined here. It will be evident that the quasi–classical setup leads to $\delta_2 = 0$. The FP–QME (27) reduces to

$$
\begin{aligned}
\dot{\rho}(t) = & -i[H_S + \hat{Q}_S\hat{x}_B, \rho(t)] - \mathcal{L}_{FP}^{HT}\hat{\rho}(t) \\
& - \delta_0[\hat{Q}_S, [\hat{p}_B, \hat{\rho}(t)]] - \delta_1[\hat{Q}_S, [\hat{x}_B, \hat{\rho}(t)]],
\end{aligned} \tag{39}
$$

with the simplified Eq. (28) that can be written for

$$
\delta_0 = \eta_+ + \eta_- - \frac{1}{\beta\Omega}, \tag{40a}
$$

$$
\delta_1 = \frac{\eta_+\gamma_1 + \eta_-\gamma_2}{\Omega} - \frac{i}{2}. \tag{40b}
$$

Involved in Eq. (39) is the classical (high–temperature) FP operator, $\mathcal{L}_{FP}^{HT}$ of Eq. (20). In comparing with Caldeira–Leggett's QME (19), two additional terms appear, each of which engages both the system action via $\hat{Q}_S$ and the solvation mode action. These are caustic terms that bridge between the full quantum description on the primary system and the classical $\mathcal{L}_{FP}^{HT}$–based description on the secondary environment influence.

Physically, the δ_0–term and δ_1–term in Eq. (39), which engage the solvation momentum $\hat{p}_B$ and coordinate $\hat{x}_B$, are related to the short–time and long–time caustics, respectively. This would suggest the so–called *integral* scheme, for the quasi–classical bath correlation function, Eq. (38), having the exact values at

$$
\eta_+ + \eta_- = \langle \hat{x}_B(t=0)\hat{x}_B(0)\rangle_B = \langle x_B^2\rangle_B, \tag{41a}
$$

$$
\frac{\eta_+}{\gamma_1} + \frac{\eta_-}{\gamma_2} = \int_0^\infty dt\, \langle \hat{x}_B(t)\hat{x}_B(0)\rangle_B. \tag{41b}
$$

The exact integral value is [cf. Eqs. (6) and (9)]

$$
\int_0^\infty dt\, \langle \hat{x}_B(t)\hat{x}_B(0)\rangle_B = \hat{C}(\omega = 0) = \frac{\zeta}{\beta\Omega^3} - \frac{i}{2\Omega}, \tag{42}
$$

for the BO model, Eq. (10), considered in this work. We obtain the integral–scheme values of Eq. (40),

$$
\delta_0^{int} = \Delta_\beta, \quad \delta_1^{int} = \Delta_\beta\zeta/\Omega, \tag{43}
$$

where

$$
\Delta_\beta \equiv \langle x_B^2\rangle_B - \langle x_B^2\rangle_B^{HT}. \tag{44}
$$

The corresponding FP–QME (39) then reads

$$
\begin{aligned}
\dot{\rho}(t) = & -i[H_S + \hat{Q}_S\hat{x}_B, \rho(t)] - \mathcal{L}_{FP}^{HT}\hat{\rho}(t) \\
& - \Delta_\beta\left\{[\hat{Q}_S, [\hat{p}_B, \hat{\rho}(t)]] + \frac{\zeta}{\Omega}[\hat{Q}_S, [\hat{x}_B, \hat{\rho}(t)]]\right\}.
\end{aligned} \tag{45}
$$

This is an appealing formalism, which modifies Caldeira–Leggett's QME (19) via only the exact value of $\Delta_\beta \equiv \langle x_B^2\rangle_B - \langle x_B^2\rangle_B^{HT}$ [Eq. (44)], to account for both the short–time and long–time caustic effects.

For comparisons at both the formal and numerical levels, consider also the so–called order-1 scheme and derivative

scheme, as follows. The order-1 scheme is related to the Taylor expansion, one more order than Eq. (18),

$$\frac{1}{1 - e^{-\beta\omega}} \approx \frac{1}{2} + \frac{1}{\beta\omega} + \frac{\beta\omega}{12}. \tag{46}$$

This leads to Eq. (38) with [cf. Eq. (41)]

$$\eta_+^{(1)} + \eta_-^{(1)} = \frac{1}{\beta\Omega} + \frac{\beta\Omega}{12}, \tag{47a}$$

$$\frac{\eta_+^{(1)}}{\gamma_1} + \frac{\eta_-^{(1)}}{\gamma_2} = -\frac{i}{2\Omega}. \tag{47b}$$

The order-1 scheme values of Eq. (40) are

$$\delta_0^{(1)} = \frac{\beta\Omega}{12}, \qquad \delta_1^{(1)} = \frac{\beta\zeta}{12}. \tag{48}$$

Note that $\delta_1^{(1)}/\delta_0^{(1)} = \delta_1^{\mathrm{int}}/\delta_0^{\mathrm{int}} = \zeta/\Omega$. The corresponding FP–QME (39) has the same form of Eq. (45), but rather with the approximated value of $\Delta_\beta \approx \beta\Omega/12$.

The derivative scheme sets the quasi–classical bath correlation function, Eq. (38), and its time–derivative to be exact at $t = 0$. Formally, it goes by Eq. (41a) but together with $\eta_+\gamma_1 + \eta_-\gamma_2 = -\langle \dot{\hat{x}}_B \hat{x}_B \rangle_B = i\Omega/2$ [cf. Eq. (23b)]. Therefore, the derivative scheme is short-time in nature, with the related values for Eq. (40a) being

$$\delta_0^{\mathrm{der}} = \Delta_\beta, \qquad \delta_1^{\mathrm{der}} = 0. \tag{49}$$

The observation here confirms the physical picture that the δ_0–term and δ_1–term in Eq. (39) do describe the short–time and long–time caustics, respectively.

The integral scheme [Eq. (41)] would perform significantly better than the order-1 and the derivative schemes, as inferred from their constructions. Figure 1 presents their
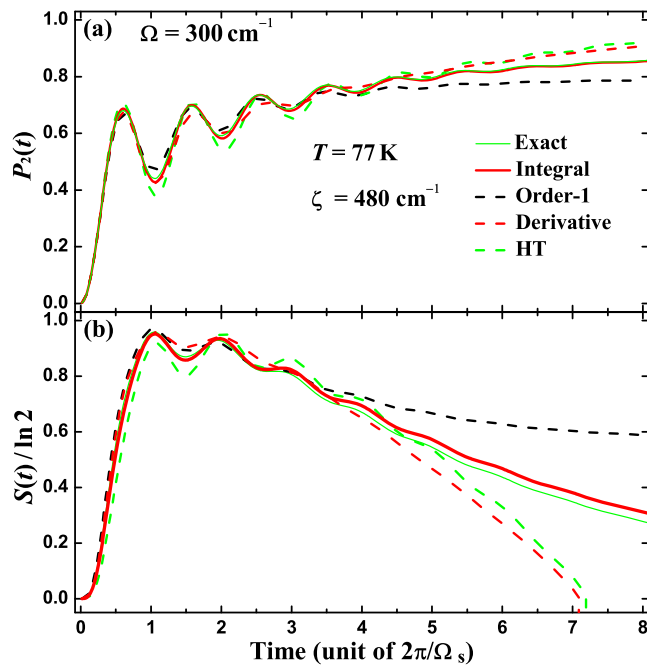

FIG. 1. Performances of quasi–classical schemes, on a two–level system evolution. (a) $P_2(t)$ the transferred population; (b) $S(t) = -\mathrm{tr}_S[\rho_S(t) \ln \rho_S(t)]$ the entropy, scaled by $S_{\max} = \ln 2$ of a two–level system. The time is in unit of bare system oscillation period. See text for the details.

performances on the dynamics of an illustrated two–level system to be soon specified. Considered here is an under-damped Brownian oscillator environment, at a moderately low temperature ($k_B T/\Omega \approx 0.18$). Apparently, the integral scheme (red) performs the best here, just almost overlaps with the converged HEOM result (thin-green). While the order-1 scheme (black–dash) is the second best here, the derivative scheme (red–dash) and the high–temperature classical scheme (green–dash) show negativity, where the entropy diverges. The illustrative system here is as follows. $H_S = \Delta\hat{\sigma}_z + V\hat{\sigma}_x$ and $\hat{Q}_S = \sqrt{2\lambda\Omega}\,\hat{\sigma}_z$, with $\Delta = V = 200$ cm^{-1} and $\lambda = 180$ cm^{-1}. Here, $\hat{\sigma}_z$ and $\hat{\sigma}_x$ are Pauli matrices. The bare system transition frequency, $\Omega_S = 2\sqrt{\Delta^2 + V^2}$, is used in relation to the time unit in Fig. 1. Other parameters are specified in the figure.

B. Semiclassical environment descriptors

The observations by now provide guidance for the development of semiclassical schemes, where the effective frequency $\bar{\Omega}$ and friction $\bar{\zeta}$ of Brownian oscillators environment are also temperature dependent. Therefore, the δ_2–term of Eq. (27) accounts for the caustic renormalization, which does not appear in quasi–classical FP–QME (39).

Physically, renormalization is concerned with the long–time property. The extended integral scheme is going to engage further the exact value of $\hat{C}'(\omega = 0) = d\hat{C}(\omega = 0)/d\omega$, with $\hat{C}(\omega)$ being defined in Eq. (6). Together with those of the integral scheme in Eq. (41), the extended integral scheme, to be called the minimum–dissipation ansatz (MDA) hereafter, goes by[30]

$$\eta_+ + \eta_- = \langle \hat{x}_B^2 \rangle_B, \tag{50a}$$

$$\frac{\eta_+}{\gamma_+} + \frac{\eta_-}{\gamma_-} = \hat{C}(\omega = 0) = \frac{\zeta}{\beta\Omega^3} - \frac{i}{\beta\Omega}, \tag{50b}$$

$$\frac{\eta_+}{\gamma_+^2} + \frac{\eta_-}{\gamma_-^2} = -i\hat{C}'(\omega = 0). \tag{50c}$$

From Eqs. (50a) and (50b), followed by using Eq. (28) that satisfies $\gamma_+\gamma_- = \bar{\Omega}^2$ and $\gamma_+ + \gamma_- = \bar{\zeta}$, we can readily obtain

$$\delta_0 = \langle \hat{x}_B^2 \rangle_B - \frac{1}{\beta\bar{\Omega}}, \quad \delta_1 = \langle \hat{x}_B^2 \rangle_B \frac{\bar{\zeta}}{\bar{\Omega}} - \frac{\zeta\bar{\Omega}}{\beta\Omega^3},$$
$$\delta_2 = \frac{\bar{\Omega}}{\Omega} - 1. \tag{51}$$

The last identity confirms that the δ_2–term in Eq. (27) describes the renormalization caustics. Interestingly, the solutions to Eq. (50) satisfy[30]

$$\frac{\bar{\zeta}}{\zeta} = \frac{\bar{\Omega}^2}{\Omega^2} = \frac{1}{Z(r_{\mathrm{BO}}, \theta)} < 1, \tag{52}$$

with the MDA characteristic function,

$$Z(r_{\mathrm{BO}}, \theta) \equiv \frac{1 + \Psi(r_{\mathrm{BO}}, \theta)}{1 + \Phi(r_{\mathrm{BO}}, \theta)}. \tag{53}$$

Here, $r_{\mathrm{BO}} \equiv \zeta/(2\Omega)$, $\theta \equiv 1/(\beta\Omega)$, and[30]

$$\Phi(r_{\mathrm{BO}}, \theta) = \sum_{m=1}^{\infty} \frac{2}{1 + 4\pi m\theta(\pi m\theta + r_{\mathrm{BO}})}, \tag{54a}$$

$$\Psi(r_{\mathrm{BO}}, \theta) = 2\sum_{m=1}^{\infty} \frac{1 + (2\pi m\theta)^2 - 4r_{\mathrm{BO}}^2 + \frac{r_{\mathrm{BO}}}{\pi m\theta}}{\left[1 + (2\pi m\theta)^2\right]^2 - (4\pi m\theta r_{\mathrm{BO}})^2}. \tag{54b}$$

They are related to the Matsubara expansions on $\langle x_B^2 \rangle_B$ and $\hat{C}'(\omega = 0)$, respectively. In fact, $\langle x_B^2 \rangle_B = \theta(1 + \Phi)$ or $\Delta_\beta = \theta\Phi$, since $\langle \hat{x}_B^2 \rangle_B^{HT} = \theta$. Comparing to Eq. (43) of the integral scheme, we recast Eq. (51) as

$$\delta_0 = \Delta_\beta + \theta(1 - \sqrt{Z}), \quad \delta_1 = \frac{\Delta_\beta \zeta}{\sqrt{Z}\Omega}, \quad \delta_2 = \frac{1}{\sqrt{Z}} - 1. \quad (55)$$

Apparently, the integral scheme assumes $Z = 1$.

Turning to the solvation bath spectrum,

$$C(\omega) \equiv \text{Re} \int_0^\infty dt\, e^{i\omega t} \langle x_B(t) x_B(0) \rangle_B = \frac{J(\omega)}{1 - e^{-\beta\omega}}. \quad (56)$$

Its MDA approximant reads[30]

$$C(\omega) \approx \left(\frac{1}{2} + \frac{1}{\beta\omega} + \theta^2 \Phi Z \beta\omega \right) \bar{J}(\omega), \quad (57)$$

with

$$\bar{J}(\omega) = \frac{\Omega \zeta \omega}{(\Omega^2 - Z\omega^2)^2 + (\zeta\omega)^2}. \quad (58)$$

The MDA bath spectrum is positive when $\omega \geq 0$, but it would be negative if

$$-\frac{1}{2} < \frac{1}{\beta\omega} + \theta^2 \Phi Z \beta\omega < 0. \quad (59)$$

The resulting negativity frequency range is

$$-\frac{1 + \sqrt{X}}{4\theta\Phi Z} < \frac{\omega}{\Omega} < -\frac{1 - \sqrt{X}}{4\theta\Phi Z}; \quad \text{with } X > 0, \quad (60)$$

where

$$X(r_{BO}, \theta) \equiv 1 - 16\theta^2 \Phi(r_{BO}, \theta) Z(r_{BO}, \theta). \quad (61)$$

When $X(r_{BO}, \theta) < 0$, the approximated bath spectrum is of $C^{app}(\omega) \geq 0$ for $-\infty < \omega < \infty$. This defines the negativity–free subspace, where $X < 0$.

Note that $Z > 1$, whereas the integral–scheme assumes $Z = 1$. Consequently, $X < X_{integral}$. Therefore, the MDA has a larger negativity–free subspace and also a smaller negativity frequency range [cf. Eq. (60)] than those of the integral scheme. The semiclassical scheme is better than the quasi–classical one.

Figure 2(a) depicts the lines of $X(r_{BO}, \theta) = 0$, for the MDA (blue) and the integral–scheme (red), respectively. Evidently, the MDA is better, with a broader negativity–free space where $X < 0$. Figures 2(b)–2(d) present the bath spectrum approximants against the exact (green) ones, at the specified values of r_{BO} and θ. The negative spectrum frequency range of Eq. (60) is specified by the pair of arrows to each corresponding curve. Note that at $(r_{BO}, \theta) = (3, 0.3)$, $X^{MDA} < 0$ and $X^{integral} > 0$ [cf. Figs. 2(a) and 2(b)]. Evidently, MDA has smaller unphysical frequency range than that of the integral scheme. The MDA bath spectra are more accurate than their integral scheme counterparts.

We have also performed the numerical least–square–fit for the bi–exponential bath correlation function, Eq. (24), subject to the constraints by Eq. (25) and $\eta_+ + \eta_-$ being real. The exact reference is Eq. (3) or its equivalence Eq. (12). The analytical MDA values, $\eta_\pm^{MDA}$ and $\gamma_\pm^{MDA}$, are used as the initial inputs. The numerical–fitted spectra (black–dash), obtained by Fourier transformation, are also included in Figs. 2(b)–2(d), for
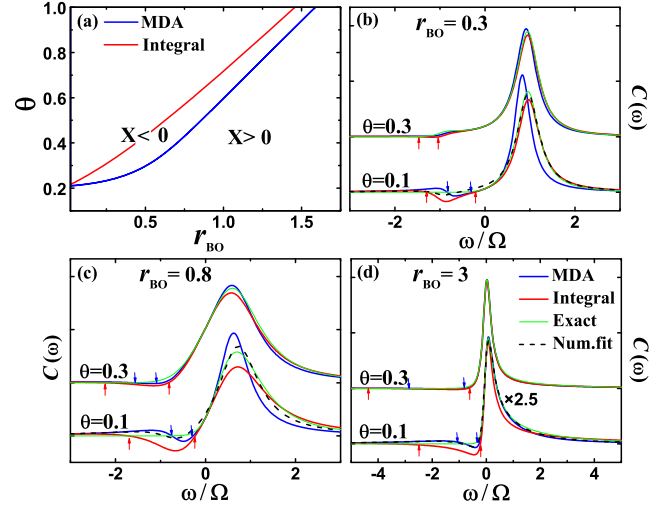

FIG. 2. (a) The bath spectrum negativity–free subspace, where $X(r_{BO}, \theta) < 0$ [Eq. (61)]. (b)–(d) The semiclassical bath spectra, with three specified values of $r_{BO} = \zeta/(2\Omega)$, at $\theta \equiv k_B T/\Omega = 0.1$ and 0.3. The pair of arrows pointing to each spectrum curve indicates the negativity frequency range [Eq. (60)].

$\theta \equiv k_B T/\Omega = 0.1$. The results for $\theta = 0.3$ are not shown here, as they practically overlap with the exact (green) ones, unless enlarged.

As anticipated, the scheme's accuracy follows "integral (red) < MDA (blue) < numerical–fit (black–dash)." However, none of these schemes work well at low temperature (about $\theta < 0.08$), indicating the breakdown of the bi–exponential approximant. Figure 3 reports the performances of these schemes on the two–level system evolutions, with $r_{BO} = 0.3$ (left panels) and $r_{BO} = 3$ (right panels), at $\theta = k_B T/\Omega = 0.1$. The corresponding bath spectra were shown in Figs. 2(b) and 2(d), respectively. At $\theta = 0.3$, all schemes perform excellently (not shown here), as inferred from their bath spectra, including the integral scheme. However, at $\theta = 0.1$, the integral (quasi–classical) scheme breaks down, whereas
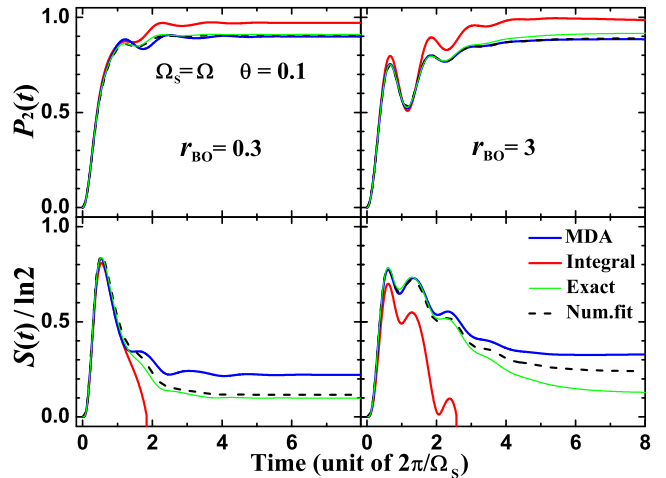

FIG. 3. Performances of the specified schemes on the dynamics of the two–level system. Upper panels: $P_2(t)$ the transferred population. Lower panels: $S(t) = -\text{tr}_S[\rho_S(t) \ln \rho_S(t)]$ the entropy, scaled by $S_{max} = \ln 2$ of a two–level system. The time is in units of bare system oscillation period. Here, $H_S = \Delta \hat{\sigma}_z + V \hat{\sigma}_x$ and $\hat{Q}_S = \sqrt{2\lambda\Omega}\, \hat{\sigma}_z$, with $\Omega = \Omega_S \equiv \sqrt{\Delta^2 + V^2}$, $\lambda = 120$ cm^{-1} and $\Delta = V = 70$ cm^{-1}.

the semiclassical ones, MDA and numerical-fit, remain satisfactory.

Apparently, the reduced system entropy evolution is rather sensitive to coherences, which may not be directly reflected in population dynamics. It is noticed that complex systems may exhibit various subtle coherences. In this case, applications within the negativity–free subspace, as depicted where $X < 0$ in Fig. 2(a) and Eq. (61), would remain reliable. We also found that the analytical negativity–free subspace is about that of the numerical–fit scheme. This will greatly facilitate the viable extension.

V. CONCLUDING REMARKS

In summary, we developed a Fokker–Planck quantum master equation (FP–QME). This mixed quantum–semiclassical theory, Eq. (27), contains three caustic dissipative terms that are missing in Caldeira–Leggett's QME (19), a type of quantum–classical method. These three terms account for the *short–time*, *long–time*, and *renormalization* caustics, respectively.

We proposed and analyzed in details the minimum–dissipation ansatz (MDA) [Eq. (50)], and validated its broad range of applicability. The integral scheme [Eq. (50)] for quasi–classical environments is recovered trivially from the MDA. The negativity–free subspace, as depicted in Fig. 2(a) and Eq. (61) for MDA, is also about that of the numerical fit scheme. Applications of the semiclassical schemes to realistic systems, with rich correlated system–and–bath coherences or entanglements, may be limited within the negativity–free subspace. While the analytical ansatz may only be available for specific model environments, the principle of minimum–dissipation ansatz is general. It is related closely to the common practice of using one or few numerically fitted exponential function(s) to analyse dynamical properties observed in experiments and simulations. The analytical MDA results,[30] including the identification of the negativity–free subspace in this work, will greatly facilitate these efforts.

We also established the equivalence between the FP–QME and the HEOM formalism,[11–16] with the same semiclassical environment. This enables the FP–QME evaluations using the established HEOM propagator techniques.[31–36] This establishment would also provide guidance toward advanced semiclassical quantum dissipation methods, at both the theoretical formulation and numerical implementation levels, for complex systems.

The proposed theory performs remarkably well on the illustrative systems, covering both underdamped and overdamped vibronic coupling dynamics, at rather low temperature. Even the quasi–classical method proposed in this work performs well. The resulting FP–QME (45) is very appealing. It modifies Caldeira–Leggett's QME (19) via only the exact value of $\Delta_\beta \equiv \langle x_B^2 \rangle_B - \langle x_B^2 \rangle_B^{\mathrm{HT}}$, but improves significantly. The modifications, which go step–by–step, are rather simple and appealing, with solid grounds and remarkable improvements. It is anticipated that the present work will benefit to the advancement of semiclassical methods for complex systems in general, where exact results are unobtainable.

APPENDIX A: FOKKER–PLANCK OPERATOR

This appendix summarizes the well–established FP operator algebra; see Ref. 26. Let us start with Eq. (31), the similarity transformation of the FP operator of Eq. (30). We obtain

$$\tilde{L}_{\mathrm{FP}} \equiv e^S \hat{L}_{\mathrm{FP}} e^{-S} = \bar{\Omega}(\hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2) + \bar{\zeta} \hat{a}_2^\dagger \hat{a}_2, \quad (A1)$$

where

$$\hat{a}_1 = \frac{\sqrt{\beta\bar{\Omega}}}{2} x_B + \frac{1}{\sqrt{\beta\bar{\Omega}}} \frac{\partial}{\partial x_B},$$
$$\hat{a}_2 = \frac{\sqrt{\beta\bar{\Omega}}}{2} p_B + \frac{1}{\sqrt{\beta\bar{\Omega}}} \frac{\partial}{\partial p_B}. \quad (A2)$$

Introduce now

$$\hat{c}_1^- \equiv r_2 \hat{a}_1 + r_1 \hat{a}_2, \qquad \hat{c}_2^- \equiv r_1 \hat{a}_1 + r_2 \hat{a}_2, \quad (A3a)$$

$$\hat{c}_1^+ \equiv -r_2 \hat{a}_1^\dagger + r_1 \hat{a}_2^\dagger, \qquad \hat{c}_2^+ \equiv r_1 \hat{a}_1^\dagger - r_2 \hat{a}_2^\dagger, \quad (A3b)$$

with r_1 and r_2 being related to $\gamma_\pm$ of Eq. (25) by

$$r_1 = \sqrt{\gamma_+/(\gamma_+ - \gamma_-)}, \quad r_2 = \sqrt{\gamma_-/(\gamma_+ - \gamma_-)}. \quad (A4)$$

The transformed FP operator, Eq. (A1), is then diagonalized as

$$\tilde{L}_{\mathrm{FP}} = \gamma_+ \hat{c}_1^+ \hat{c}_1^- + \gamma_- \hat{c}_2^+ \hat{c}_2^-. \quad (A5)$$

It is easy to verify that despite $\hat{c}_j^\pm \neq (\hat{c}_j^\mp)^\dagger$, they satisfy the boson-like relations

$$[\hat{c}_j^-, \hat{c}_k^+] = \delta_{jk} \text{ and } [\hat{c}_j^\pm, \hat{c}_k^\pm] = 0. \quad (A6)$$

Consequently, the eigenvalue problem for the non-Hermitian $\hat{c}_j^+ \hat{c}_j^-$ operator follows also the harmonic oscillator algebra.[26] We obtain

$$\hat{c}_j^- \psi_{n_j}(x_B, p_B) = \sqrt{n_j}\, \psi_{n_j-1}(x_B, p_B), \quad (A7a)$$

$$\hat{c}_j^+ \psi_{n_j}(x_B, p_B) = \sqrt{n_j + 1}\, \psi_{n_j+1}(x_B, p_B), \quad (A7b)$$

where $n_j = 0, 1, ...$, and further

$$(\hat{c}_j^+ \hat{c}_j^-) \psi_{n_j}(x_B, p_B) = n_j \psi_{n_j}(x_B, p_B). \quad (A8)$$

The ground state satisfies $\hat{c}_j^- \psi_0(x_B, p_B) = 0$. Having $\hat{c}_j^-$ defined in Eq. (A3) with Eq. (A2), we obtain the normalized ground state wavefunction,

$$\psi_0(x_B, p_B) = \left(\frac{\beta\bar{\Omega}}{2\pi}\right)^{\frac{1}{2}} e^{-\frac{\beta\bar{\Omega}}{4}(x_B^2 + p_B^2)}. \quad (A9)$$

Together with Eq. (A7b), we obtain

$$\psi_{n_j}(x_B, p_B) = \frac{1}{\sqrt{n_j!}} (\hat{c}_j^+)^{n_j} \psi_0(x_B, p_B); \quad n_j = 0, 1, 2, ...,$$

for

$$\hat{c}_j^+ \hat{c}_j^- \psi_{n_j}(x_B, p_B) = n_j \psi_{n_j}(x_B, p_B). \quad (A10)$$

The eigenfunctions for $\tilde{L}_{\text{FP}}$ of Eq. (A5) are then

$$\Psi_{n_1 n_2}(x_{\text{B}}, p_{\text{B}}) \equiv \psi_{n_1}(x_{\text{B}}, p_{\text{B}}) \psi_{n_2}(x_{\text{B}}, p_{\text{B}}), \qquad \text{(A11)}$$

by which

$$\tilde{L}_{\text{FP}} \Psi_{n_1 n_2} = (n_1 \gamma_+ + n_2 \gamma_-) \Psi_{n_1 n_2}. \qquad \text{(A12)}$$

This is Eq. (32).

For completeness, consider below the orthonormality of $\{\Psi_{n_1 n_2}(x_{\text{B}}, p_{\text{B}})\}$, which reads[26]

$$\langle \bar{\Psi}_{n_1 n_2} | \Psi_{n_1' n_2'} \rangle \equiv \int \int dx_{\text{B}} dp_{\text{B}} \bar{\Psi}^*_{n_1 n_2}(x_{\text{B}}, p_{\text{B}}) \Psi_{n_1' n_2'}(x_{\text{B}}, p_{\text{B}})$$
$$= \delta_{n_1 n_1'} \delta_{n_2 n_2'}. \qquad \text{(A13)}$$

Here $\{\bar{\Psi}_{n_1 n_2}(x_{\text{B}}, p_{\text{B}})\}$ are the eigenfunctions of the non–Hermitian operator $\tilde{L}^\dagger_{\text{FP}}$, satisfying [cf. Eq. (A12)]

$$\tilde{L}^\dagger_{\text{FP}} \bar{\Psi}_{n_1 n_2} = (n_1 \gamma^*_+ + n_2 \gamma^*_-) \bar{\Psi}_{n_1 n_2}. \qquad \text{(A14)}$$

To proceed, we denote $\bar{c}^\pm_j \equiv (\hat{c}^\mp_j)^\dagger$ [cf. Eq. (A3)],

$$\begin{array}{ll} \bar{c}^+_1 \equiv r^*_2 \hat{a}^\dagger_1 + r^*_1 \hat{a}^\dagger_2, & \bar{c}^-_1 \equiv -r^*_2 \hat{a}_1 + r^*_1 \hat{a}_2, \\ \bar{c}^+_2 \equiv r^*_1 \hat{a}^\dagger_1 + r^*_2 \hat{a}^\dagger_2, & \bar{c}^-_2 \equiv r^*_1 \hat{a}_1 - r^*_2 \hat{a}_2. \end{array} \qquad \text{(A15)}$$

The Hermitian conjugate to Eq. (A5) is then

$$\tilde{L}^\dagger_{\text{FP}} = \gamma^*_+ \bar{c}^+_1 \bar{c}^-_1 + \gamma^*_- \bar{c}^+_2 \bar{c}^-_2. \qquad \text{(A16)}$$

It is easy to show that $[\bar{c}^-_j, \bar{c}^+_k] = \delta_{jk}$ and $[\bar{c}^\pm_j, \bar{c}^\pm_k] = 0$. The eigen problem for $\tilde{L}^\dagger_{\text{FP}}$ can then be addressed with the harmonic oscillator algebra as Eqs. (A7)–(A11). We obtain

$$\bar{\Psi}_{n_1 n_2}(x_{\text{B}}, p_{\text{B}}) = \bar{\psi}_{n_1}(x_{\text{B}}, p_{\text{B}}) \bar{\psi}_{n_2}(x_{\text{B}}, p_{\text{B}}), \qquad \text{(A17)}$$

where

$$\bar{\psi}_{n_j}(x_{\text{B}}, p_{\text{B}}) = \frac{1}{\sqrt{n_j!}} (\bar{c}^+_j)^{n_j} \psi_0(x_{\text{B}}, p_{\text{B}}). \qquad \text{(A18)}$$

The ground state wavefunction, $\psi_0(x_{\text{B}}, p_{\text{B}})$, remains in the same form of Eq. (A9).

APPENDIX B: DERIVATIONS OF FP–QME (27)

1. Some useful relations

To facilitate the construction of FP–QME in the second part of this appendix, we present here some directly useful relations. Naturally, we consider the S–transformation–space quantities, with $S = \frac{1}{4} \beta \bar{\Omega}(x^2_{\text{B}} + p^2_{\text{B}})$ having been defined in Eq. (31). In the S–transformation space, Eq. (35) reads

$$\tilde{\rho}_{\text{W}}(p_{\text{B}}, x_{\text{B}}, t) \equiv e^S \rho_{\text{W}}(p_{\text{B}}, x_{\text{B}}, t)$$
$$= \sum_{n_1, n_2} \frac{s_{n_1 n_2}}{\sqrt{n_1! n_2!}} \rho_{n_1 n_2}(t) \Psi_{n_1 n_2}(x_{\text{B}}, p_{\text{B}}). \qquad \text{(B1)}$$

As inferred from Eq. (A12), we have

$$\tilde{L}_{\text{FP}} \tilde{\rho}_{\text{W}} = \sum_{n_1, n_2} \frac{s_{n_1 n_2}}{\sqrt{n_1! n_2!}} (n_1 \gamma_+ + n_2 \gamma_-) \rho_{n_1 n_2} \Psi_{n_1 n_2}. \qquad \text{(B2)}$$

Besides $\tilde{L}_{\text{FP}} \equiv e^S \hat{L}_{\text{FP}} e^{-S}$, we will also treat the S–transformations on other basic operators in the FP-QME. Denote for book-keeping hereafter [cf. Eq. (31)]

$$(\hat{O})_S \equiv e^S \hat{O} e^{-S} = e^{\beta \bar{\Omega}(x^2_{\text{B}} + p^2_{\text{B}})/4} \hat{O} e^{-\beta \bar{\Omega}(x^2_{\text{B}} + p^2_{\text{B}})/4}. \qquad \text{(B3)}$$

Together with Eqs. (A2) and (A3), we obtain

$$\sqrt{\beta \bar{\Omega}} \left(x_{\text{B}} + \frac{1}{\beta \bar{\Omega} \partial x_{\text{B}}} \right)_S = \hat{a}_1 = -r_2 \hat{c}^-_1 + r_1 \hat{c}^-_2,$$
$$\sqrt{\beta \bar{\Omega}} \left(p_{\text{B}} + \frac{1}{\beta \bar{\Omega} \partial p_{\text{B}}} \right)_S = \hat{a}_2 = r_1 \hat{c}^-_1 - r_2 \hat{c}^-_2; \qquad \text{(B4)}$$

and

$$-\frac{1}{\sqrt{\beta \bar{\Omega}}} \left(\frac{\partial}{\partial x_{\text{B}}} \right)_S = \hat{a}^\dagger_1 = r_2 \hat{c}^+_1 + r_1 \hat{c}^+_2,$$
$$-\frac{1}{\sqrt{\beta \bar{\Omega}}} \left(\frac{\partial}{\partial p_{\text{B}}} \right)_S = \hat{a}^\dagger_2 = r_1 \hat{c}^+_1 + r_2 \hat{c}^+_2. \qquad \text{(B5)}$$

Turn to the notation $\bar{\eta}_\pm$ of Eq. (34). For the semiclassical bath correlation function, Eq. (24), the time–reversal relation, Eq. (5), can be expressed with this notation as

$$\bar{\eta}^*_+ e^{-\gamma_+ t} + \bar{\eta}^*_- e^{-\gamma_- t} = (\eta_+ e^{-\gamma_+ t} + \eta_- e^{-\gamma_- t})^*. \qquad \text{(B6)}$$

Taking the time derivative at $t = 0$, we obtain

$$\bar{\eta}^*_+ \gamma_+ + \bar{\eta}^*_- \gamma_- = (\eta_+ \gamma_+ + \eta_- \gamma_-)^*. \qquad \text{(B7)}$$

Together with $r_1/r_2 = \gamma_+/\bar{\Omega}$ and $r_2/r_1 = \gamma_-/\bar{\Omega}$, as inferred from Eqs. (A4) and (25), we have

$$\bar{\eta}^*_+ \frac{r_1}{r_2} + \bar{\eta}^*_- \frac{r_2}{r_1} = \left(\eta_+ \frac{r_1}{r_2} + \eta_- \frac{r_2}{r_1} \right)^* = \delta_1 - \frac{i}{2}(1 + \delta_2). \qquad \text{(B8)}$$

This last identity was obtained via Eq. (28b).

2. Derivation of the FP–QME

In the following we exploit Eqs. (33)–(35) to derive the corresponding FP–QME (29). Taking the time derivative on Eq. (B1), the S–transformation of Eq. (35), followed by using Eqs. (33) and (B2), we obtain

$$\frac{\partial}{\partial t} \tilde{\rho}_{\text{W}} = \sum_{n_1, n_2} \frac{s_{n_1 n_2}}{\sqrt{n_1! n_2!}} \dot{\rho}_{n_1 n_2} \Psi_{n_1 n_2}$$
$$= -(i\mathcal{L}_{\text{S}} + \tilde{L}_{\text{FP}}) \tilde{\rho}_{\text{W}} - i([\text{I}] + [\text{II}]). \qquad \text{(B9)}$$

The first term, the term–[I], and the term–[II] above arise from the first, second, and the remaining terms in Eq. (33), respectively,

$$[\text{I}] = \sum_{n_1, n_2} \frac{s_{n_1 n_2}}{\sqrt{n_1! n_2!}} [\hat{Q}_{\text{S}}, \rho_{n_1+1, n_2} + \rho_{n_1, n_2+1}] \Psi_{n_1 n_2}$$
$$= \sum_{n_1, n_2} \frac{s_{n_1-1, n_2}}{\sqrt{(n_1-1)! n_2!}} [\hat{Q}_{\text{S}}, \rho_{n_1 n_2}] \Psi_{n_1-1, n_2}$$
$$+ \sum_{n_1, n_2} \frac{s_{n_1, n_2-1}}{\sqrt{n_1! (n_2-1)!}} [\hat{Q}_{\text{S}}, \rho_{n_1 n_2}] \Psi_{n_1, n_2-1}. \qquad \text{(B10)}$$

With the identities [cf. Eqs. (A7) and (A11)],

$$\begin{array}{l} \hat{c}^-_1 \Psi_{n_1 n_2} = \sqrt{n_1} \Psi_{n_1-1, n_2}, \\ \hat{c}^-_2 \Psi_{n_1 n_2} = \sqrt{n_2} \Psi_{n_1, n_2-1}, \end{array} \qquad \text{(B11)}$$

and also [cf. Eq. (36)]

$$\begin{array}{l} \sqrt{\beta \bar{\Omega}} \, s_{n_1 n_2} = -r_2 s_{n_1+1 n_2}, \\ \sqrt{\beta \bar{\Omega}} \, s_{n_1, n_2} = r_1 s_{n_1, n_2+1}, \end{array} \qquad \text{(B12)}$$

we evaluate Eq. (B10) as

$$
\begin{aligned}
[\mathrm{I}] &= \frac{1}{\sqrt{\beta\bar\Omega}} \sum_{n_1,n_2} \frac{-r_2 s_{n_1,n_2}}{\sqrt{n_1!\,n_2!}} [\hat Q_{\mathrm S}, \rho_{n_1 n_2}](\hat c_1^- \Psi_{n_1 n_2}) \\
&+ \frac{1}{\sqrt{\beta\bar\Omega}} \sum_{n_1,n_2} \frac{r_1 s_{n_1,n_2}}{\sqrt{n_1!\,n_2!}} [\hat Q_{\mathrm S}, \rho_{n_1 n_2}](\hat c_2^- \Psi_{n_1 n_2}) \\
&= \frac{-r_2 \hat c_1^- + r_1 \hat c_2^-}{\sqrt{\beta\bar\Omega}} [\hat Q_{\mathrm S}, \tilde\rho_{\mathrm W}] = \Big(x_{\mathrm B} + \frac{1}{\beta\bar\Omega \partial x_{\mathrm B}}\Big)_S [\hat Q_{\mathrm S}, \tilde\rho_{\mathrm W}].
\end{aligned}
$$
(B13)

The last two expressions were obtained by using Eqs. (B1) and (B4), respectively.

Similarly, the term–[II] in Eq. (B9), which arises from the last two terms in Eq. (33), is evaluated as follows:

$$
\begin{aligned}
[\mathrm{II}] &= \sum_{n_1,n_2} \Bigg\{ \frac{s_{n_1 n_2}}{\sqrt{n_1!\,n_2!}} \Big[n_1\big(\eta_+ \hat Q_{\mathrm S} \rho_{n_1-1,n_2} - \bar\eta_+^* \rho_{n_1-1,n_2} \hat Q_{\mathrm S}\big) \\
&+ n_2\big(\eta_- \hat Q_{\mathrm S} \rho_{n_1,n_2-1} - \bar\eta_-^* \rho_{n_1,n_2-1} \hat Q_{\mathrm S}\big) \Big] \Bigg\} \Psi_{n_1 n_2} \\
&= \sum_{n_1,n_2} \Bigg[\frac{s_{n_1+1,n_2}}{\sqrt{n_1!\,n_2!}} (\eta_+ \hat Q_{\mathrm S} \rho_{n_1 n_2} - \bar\eta_+^* \rho_{n_1 n_2} \hat Q_{\mathrm S})(\hat c_1^+ \Psi_{n_1 n_2}) \\
&+ \frac{s_{n_1,n_2+1}}{\sqrt{n_1!\,n_2!}} (\eta_- \hat Q_{\mathrm S} \rho_{n_1 n_2} - \bar\eta_-^* \rho_{n_1 n_2} \hat Q_{\mathrm S})(\hat c_2^+ \Psi_{n_1 n_2}) \Bigg] \\
&= \sqrt{\beta\bar\Omega}\Big[\Big(-\frac{\eta_+}{r_2}\hat c_1^+ + \frac{\eta_-}{r_1}\hat c_2^+\Big)\hat Q_{\mathrm S} \tilde\rho_{\mathrm w} \\
&+ \Big(\frac{\bar\eta_+^*}{r_2}\hat c_1^+ - \frac{\bar\eta_-^*}{r_1}\hat c_2^+\Big)\tilde\rho_{\mathrm w} \hat Q_{\mathrm S}\Big].
\end{aligned}
$$
(B14)

The last identity was obtained by using Eqs. (B12) and (B1). The quantities in the last two parentheses above are evaluated by using Eq. (A3), followed by Eq. (B6) at $t = 0$ and Eq. (B8), we have

$$
\begin{aligned}
-\frac{\eta_+}{r_2}\hat c_1^+ + \frac{\eta_-}{r_1}\hat c_2^+ &= \frac{\eta_+}{r_2}(r_2 \hat a_1^\dagger - r_1 \hat a_2^\dagger) + \frac{\eta_-}{r_1}(r_1 \hat a_1^\dagger - r_2 \hat a_2^\dagger) \\
&= (\eta_+ + \eta_-)\hat a_1^\dagger - \Big(\eta_+ \frac{r_1}{r_2} + \eta_- \frac{r_2}{r_1}\Big)\hat a_2^\dagger \\
&= (\eta_+ + \eta_-)\hat a_1^\dagger - \Big[\delta_1 + \frac{i}{2}(1+\delta_2)\Big]\hat a_2^\dagger
\end{aligned}
$$
(B15a)

and

$$
\begin{aligned}
\frac{\bar\eta_+^*}{r_2}\hat c_1^+ - \frac{\bar\eta_-^*}{r_1}\hat c_2^+ &= \frac{\bar\eta_+^*}{r_2}(-r_2 \hat a_1^\dagger + r_1 \hat a_2^\dagger) - \frac{\bar\eta_-^*}{r_1}(r_1 \hat a_1^\dagger - r_2 \hat a_2^\dagger) \\
&= -(\bar\eta_+^* + \bar\eta_-^*)\hat a_1^\dagger + \Big(\bar\eta_+^* \frac{r_1}{r_2} + \bar\eta_-^* \frac{r_2}{r_1}\Big)\hat a_2^\dagger \\
&= -(\eta_+ + \eta_-)\hat a_1^\dagger + \Big[\delta_1 - \frac{i}{2}(1+\delta_2)\Big]\hat a_2^\dagger.
\end{aligned}
$$
(B15b)

Note that $\bar\eta_+ + \bar\eta_+ = \eta_+ + \eta_- > 0$, in relation to the value of $\langle x_{\mathrm B}^2\rangle_{\mathrm B}$. Together with Eq. (B5), we obtain Eq. (B14) the final expression,

$$
\begin{aligned}
[\mathrm{II}] &= -(\eta_+ + \eta_-)\Big(\frac{\partial}{\partial x_{\mathrm B}}\Big)_S [\hat Q_{\mathrm S}, \tilde\rho_{\mathrm W}] + \delta_1\Big(\frac{\partial}{\partial p_{\mathrm B}}\Big)_S [\hat Q_{\mathrm S}, \tilde\rho_{\mathrm W}] \\
&+ \frac{i}{2}(1+\delta_2)\Big(\frac{\partial}{\partial p_{\mathrm B}}\Big)_S \{\hat Q_{\mathrm S}, \tilde\rho_{\mathrm W}\}.
\end{aligned}
$$
(B16)

Substituting Eqs. (B13) and (B16) for Eq. (B9), and expressing the final result in terms of the original, untransformed Wigner–representation quantities, we obtain

$$
\begin{aligned}
\frac{\partial}{\partial t}\rho_{\mathrm W} &= -(i\mathcal L_{\mathrm S} + \hat L_{\mathrm{FP}})\rho_{\mathrm W} \\
&- i[\hat Q_{\mathrm S}, x_{\mathrm B}\rho_{\mathrm W}] + \frac{1+\delta_2}{2}\Big\{\hat Q_{\mathrm S}, \frac{\partial}{\partial p_{\mathrm B}}\rho_{\mathrm W}\Big\} \\
&+ i\delta_0\Big[\hat Q_{\mathrm S}, \frac{\partial}{\partial x_{\mathrm B}}\rho_{\mathrm W}\Big] - i\delta_1\Big[\hat Q_{\mathrm S}, \frac{\partial}{\partial p_{\mathrm B}}\rho_{\mathrm W}\Big].
\end{aligned}
$$
(B17)

This is just Eq. (29), the solvation–subspace Wigner representation of FP-QME (27), with $\delta_0 = \eta_+ + \eta_- - \frac{1}{\beta\bar\Omega}$ being defined in Eq. (28a), while δ_1 and δ_2 via the real and imaginary part of Eq. (28b), respectively.

[1] A. A. Golosov, R. A. Friesner, and P. Pechukas, J. Chem. Phys. **112**, 2095 (2000).

[2] M. Thoss, H. B. Wang, and W. H. Miller, J. Chem. Phys. **115**, 2991 (2001).

[3] A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985).

[4] L. D. Zusman, Chem. Phys. **49**, 295 (1980).

[5] L. D. Zusman, Chem. Phys. **80**, 29 (1983).

[6] A. O. Caldeira and A. J. Leggett, Physica A **121**, 587 (1983).

[7] R. Kapral and G. Ciccotti, J. Chem. Phys. **111**, 8919 (1999).

[8] G. Grunwald and R. Kapral, J. Chem. Phys. **126**, 114109 (2007).

[9] A. A. Neufeld, J. Chem. Phys. **119**, 2488 (2003).

[10] H. Nakamura, S. Nanbu, Y. Teranishi, and A. Ohta, Phys. Chem. Chem. Phys. **18**, 11972 (2016).

[11] Y. Tanimura, Phys. Rev. A **41**, 6676 (1990).

[12] Y. Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006).

[13] R. X. Xu, P. Cui, X. Q. Li, Y. Mo, and Y. J. Yan, J. Chem. Phys. **122**, 041103 (2005).

[14] R. X. Xu and Y. J. Yan, Phys. Rev. E **75**, 031107 (2007).

[15] Y. A. Yan, F. Yang, Y. Liu, and J. S. Shao, Chem. Phys. Lett. **395**, 216 (2004).

[16] J. S. Jin, X. Zheng, and Y. J. Yan, J. Chem. Phys. **128**, 234703 (2008).

[17] Q. Shi, L. P. Chen, G. J. Nan, R. X. Xu, and Y. J. Yan, J. Chem. Phys. **130**, 164518 (2009).

[18] R. X. Xu, B. L. Tian, J. Xu, Q. Shi, and Y. J. Yan, J. Chem. Phys. **131**, 214111 (2009).

[19] H. D. Zhang, J. Xu, R. X. Xu, and Y. J. Yan, in *Reaction Rate Constant Computations: Theories and Applications*, RSC Theoretical and Computational Chemistry Series No. 6, edited by K.-L. Han and T.-S. Chu (RSC, London, 2014), Chap. 13, pp. 319–336.

[20] Y. J. Yan and R. X. Xu, Annu. Rev. Phys. Chem. **56**, 187 (2005).

[21] U. Weiss, *Quantum Dissipative Systems*, Series in Modern Condensed Matter Physics, 3rd ed. (World Scientific, Singapore, 2008), Vol. 13.

[22] R. P. Feynman and F. L. Vernon, Jr., Ann. Phys. **24**, 118 (1963).

[23] A. O. Caldeira and A. J. Leggett, Ann. Phys. **149**, 374 (1983); Erratum, **153**, 445 (1984).

[24] J. Cao, J. Chem. Phys. **107**, 3204 (1997).

[25] Y. J. Yan, Phys. Rev. A **58**, 2721 (1998).

[26] H. Risken, *The Fokker-Planck Equation, Methods of Solution and Applications*, 2nd ed. (Springer-Verlag, Berlin, 1989).

[27] J. J. Ding, R. X. Xu, and Y. J. Yan, J. Chem. Phys. **136**, 224103 (2012).

[28] Y. J. Yan, J. Chem. Phys. **140**, 054105 (2014).

[29] Y. J. Yan, J. S. Jin, R. X. Xu, and X. Zheng, Front. Phys. **11**, 110306 (2016).

[30] J. J. Ding, H. D. Zhang, Y. Wang, R. X. Xu, X. Zheng, and Y. J. Yan, J. Chem. Phys. **145**, 204110 (2016).

[31] Q. Shi, L. P. Chen, G. J. Nan, R. X. Xu, and Y. J. Yan, J. Chem. Phys. **130**, 084105 (2009).

[32] B. Hein, C. Kreisbeck, T. Kramer, and M. Rodríguez, New J. Phys. **14**, 023018 (2012).

[33] C. Kreisbeck, T. Kramer, M. Rodríguez, and B. Hein, J. Chem. Theory Comput. **7**, 2166 (2011).

[34] D. Hou, S. K. Wang, R. L. Wang, L. Z. Ye, R. X. Xu, X. Zheng, and Y. J. Yan, J. Chem. Phys. **142**, 104112 (2015).

[35] H. D. Zhang and Y. J. Yan, J. Chem. Phys. **143**, 214112 (2015).

[36] L. Z. Ye, X. L. Wang, D. Hou, R. X. Xu, X. Zheng, and Y. J. Yan, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **6**, 608–638 (2016).