A phase-space study of Bloch–Redfield theory

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A phase-space representation of Bloch–Redfield theory is used to describe the dynamical evolution of quantum dissipative systems. The resulting Liouville operator equations are capable of incorporating both the master equation in eigenstate space and the stochastic equation in classical phase space, and thus provide a useful framework for mixing classical, semiclassical, and quantum dynamics for simulating complicated dissipative systems. In addition, the proper limit of quantum dissipation, the approximate nature of the second-order cumulant truncation, the detailed balance of quantum correlation functions, and the reduction of dissipation by a transformation of the bath Hamiltonian are investigated within the framework of phase-space Bloch–Redfield theory. © *1997 American Institute of Physics.* [S0021-9606(97)52032-0]

I. INTRODUCTION

In condensed phase chemistry, the competition between vibrational relaxation and activated barrier crossing or curve crossing is a major factor which determines the mechanism of a chemical process.[1,2] Take the example of photoinduced electron transfer, where a photon induces a coherent wave packet on the excited state surface, which is quickly dephased and dissipated. After the molecular system reaches thermal equilibrium, the excited state population decays exponentially due to curve crossing. Because of the fact that vibrational relaxation happens much faster than electron transfer, the dynamics becomes a well-defined rate process described by electron transfer theory. However, if vibrational relaxation is not much faster than electron transfer, then curve crossing happens before the thermal equilibrium is reached. As a result, the rate description is no longer valid. Indeed, recent progress in ultrafast spectroscopy[3–5] reveals that a laser-induced wave packet dynamical process is often the interplay of coherence, dephasing, energy relaxation, and curve crossing in a dissipative environment. Therefore, the theoretical description of such a complicated relaxation process poses a major challenge to theorists.

The formal definition of dissipation can be rigorously derived from a reduced description of dynamics.[6,7] A practical approach is to isolate the system of interest, to treat the other coordinates as a thermal bath, and to approximate the system–bath interaction as dissipation. Loosely speaking, dissipation is defined as the stochastic noise on deterministic dynamics. Therefore, the separation of system and bath is not arbitrary: One should include into the system all the coordinates involved in the deterministic dynamics. For a solvated molecule, these include all the intramolecular modes and maybe the first solvation shell. Then, such a separation of system and bath is physically adequate for many chemical processes.

The standard relaxation theory is the Bloch–Redfield theory, which consists of a set of master equations in the eigenstate space of the system.[8–23] The master equation description is based on the assumption that the relaxation process happens on a time scale much slower than the motion of the thermal bath.[24] The fast bath condition, i.e., the Markovian assumption, is easily satisfied in nuclear magnetic resonance[25] (NMR) but not for the optical excitation of large molecules which relax on the picosecond time scale. A more challenging problem arises from the eigenstate representation of the master equation and the tensor algebra involved in the evaluation of the relaxation coefficients. As a result, one can deal at most with a few spins, as in NMR, and with low-dimensional systems such as diatomic molecules. However, as discussed earlier, the number of degrees of freedom to be included in the system explicitly can be significantly larger than two. This is a fundamental limitation of the Bloch–Redfield equation when applied to optical excitation. Fortunately, in most large molecules, only a small number of degrees of freedom are considered as quantum mechanical and the rest can be handled as classical. Then, the classical degrees of freedom can be described by the Fokker–Planck equation, or equivalently, the Langevin equation. For this purpose, the eigenstate representation of the Bloch–Redfield equation is not an adequate framework for incorporating classical dissipative dynamics; instead we should remove the fast bath assumption and formulate Bloch–Redfield theory in the space of momenta and coordinates.

This work has also been stimulated by recent interest in both the theoretical and applied aspects of the Bloch–Redfield equation.[26–41] Although the use of the Bloch–Redfield equation in condensed phase spectroscopy is not nearly as popular as in NMR, for the reasons argued earlier, for limited computational resources the approach remains the method of choice and has been adopted in several studies.[33,39] For example, electron transfer is often modeled as a two-level or three-level Redfield problem.[36] Along with these new applications, advanced numerical techniques allow applications of the Redfield theory to a large number of eigenstates.[37,38] For an open Markovian quantum system, a general mathematical form of the quantum dissipative equation has been derived by virtue of the semigroup transformation method.[42] Numerical algorithms for propagating these types of quantum operator equations have been implemented.[43] Comparison of the Bloch–Redfield equation with other quantum dissipative theories has also been carried out for the quantum Brownian oscillator model.[44,45] In a companion paper, a numerical study of this new theory, along with the Bloch equation and the generalized Langevin equation, has been performed for a dissipative Morse oscillator.[46]

This paper is organized as follows: The phase-space representation of Bloch–Redfield theory is presented in Sec. II, then several aspects of the theory are discussed in Sec. III, and a summary concludes the paper in Sec. IV.

II. THEORY

A. Reduced Liouville equation of motion

Consider the composite system–bath Hamiltonian

$$H=H_0(q)+H_b(x)+V_{\rm int}(q,x), \tag{2.1}$$

where $H_0(q)$ and $H_b(x)$ are the system and bath Hamiltonians, respectively, and $V_{\rm int}(q,x)$ is the interaction between the system and the bath. The total density matrix of the system and bath obeys the Liouville equation of motion.[47]

$$\dot{\sigma}(t)=-i\mathscr{L}(t)\sigma(t), \tag{2.2}$$

where the Liouville operator is defined by

$$\mathscr{L}O=\frac{1}{\hbar}[H,O], \tag{2.3}$$

with commutator $[A,B]=AB-BA$. Equation (2.2) can be recast in the interaction picture as

$$\dot{\sigma}_I(t)=-i\mathscr{L}_I(t)\sigma_I(t), \tag{2.4}$$

where

$$\sigma_I(t)=e^{i(H_0+H_b)/\hbar}\sigma(t)e^{-i(H_0+H_b)/\hbar}, \tag{2.5}$$

and

$$\mathscr{L}_I(t)=e^{i(H_0+H_b)}\mathscr{L}_{\rm int}e^{-i(H_0+H_b)}, \tag{2.6}$$

with $\mathscr{L}_{\rm int}O=[V_{\rm int},O]/\hbar$. Formally, the solution to Eq. (2.4) can be expressed as

$$\sigma_I(t)=\exp_+\left[-i\int_0^t\mathscr{L}_I(t')dt'\right]\sigma_I(0), \tag{2.7}$$

where the subscript + denotes the time-ordering of the Liouville operators.

Following the prescription of the reduced description, we define the reduced density matrix for the system of interest as

$$\rho(t)={\rm Tr}_b\sigma(t), \tag{2.8}$$

where ${\rm Tr}_b$ means that a trace is performed over the bath degrees of freedom. Assuming that the system–bath interaction is turned off until $t=0$, we can impose the initial condition

$$\sigma(0)=\rho_b(0)\rho(0), \tag{2.9}$$

implying that there is no correlation between system and bath at the initial time. As a result, the formal solution in Eq. (2.7) can be rewritten as

$$\rho_I(t)=\left\langle\exp_+\left[-i\int_0^t\mathscr{L}_I(t')dt'\right]\rho_I(0)\right\rangle_b, \tag{2.10}$$

where the bath average is defined as

$$\langle O\rangle_b=\frac{{\rm Tr}_0O\rho_b(0)}{{\rm Tr}_b\rho_b(0)}. \tag{2.11}$$

We further assume that the interaction is within the linear regime such that a second-order truncation in the cumulant expansion of the bath average is sufficiently accurate. Consequently, the formal solution in Eq. (2.7) becomes

$$\rho_I(t)=\exp_+\left[-\int_0^t\int_0^{t'}dt'\,dt''\langle\mathscr{L}_I(t')\mathscr{L}_I(t'')\rangle_b\right]\rho_I(0), \tag{2.12}$$

which can be recast as a differential-integral equation

$$\dot{\rho}_I(t)=-\int_0^t\langle\mathscr{L}_I(t)\mathscr{L}_I(t')\rangle_b\rho_I(t')dt'. \tag{2.13}$$

This reduced Liouville equation for the dissipative system is the starting point of Redfield's analysis and has been derived in various contexts.[10,48]

B. Phase-space Bloch–Redfield theory

The interaction potential term in Eq. (2.1) can always be expanded as

$$V_{\rm int}(q,x)=\sum_j F_j(x)Q_j(q). \tag{2.14}$$

In the rest of the paper, the index j and the summation over j will be omitted for simplicity. It is convenient for further analysis to introduce the force-force correlation function as

$$C_>(t-t')=\langle F(t)F(t')\rangle_b, \tag{2.15}$$

and its complex conjugate as $C_<(t-t')=C_>^*(t-t')$, where $F(t)$ is a Heisenberg operator evolving under the bath Hamiltonian H_b.

With these notations, the second-order commutator in Eq. (2.13) can be explicitly resolved, giving

$$\begin{aligned}\langle\mathscr{L}_I(t)\mathscr{L}_I(t')\rho_I(t')\rangle_b&\\ &=\frac{1}{\hbar^2}\langle[V_I(t),[V_I(t'),\rho_I(t')]]\rangle_b\\ &=\frac{1}{\hbar^2}\langle[Q_I(t),Q_I(t')\rho_I(t')C_>(t-t')\\ &\quad-\rho_I(t')Q_I(t')C_<(t-t')]\rangle_b.\end{aligned} \tag{2.16}$$

Then, the reduced Liouville equation of Eq. (2.13) becomes

$$\dot{\rho}(t)=-i\mathscr{L}_0\rho(t)-[Q,G_>(t)-G_<(t)], \tag{2.17}$$

where the quantum dissipation term is defined by

$$G_>(t)=\frac{1}{\hbar^2}\int_0^t e^{-iH_0(t-t')/\hbar}Q\rho(t')\times e^{-iH_0(t-t')/\hbar}C_>(t-t')dt', \tag{2.18}$$

and its Hermitian conjugate $G_<(t)=G_>^+(t)$. The above expressions constitute a phase-space formulation of Redfield theory, which in the specific limit leads to the Bloch equation.[48] Two key approximations underlying the Bloch equation are to extend the upper limit of the time integral to the infinity and to replace $\rho(t')$ by $\rho(t)$ in the above integral. In addition, the rotating-wave-approximation, i.e., the secular approximation, is introduced in eigenstate space to yield the master equation.[10] Thereby removing these approximations is a major advantage of the general Redfield analysis over the Bloch equation.

To proceed, taking the time derivative of $G_>$, we have

$$\dot{G}_>(t)=Q\rho(t)C_>(0)-i\mathscr{L}_0G_>(t)+\int_0^t e^{-iH_0(t-t_0)/\hbar}Q\rho(t')e^{iH_0(t-t_0)/\hbar}\dot{C}_>(t-t')dt'. \tag{2.19}$$

The convolution integral for the quantum dissipation term in the above equation is not a convenient form for our purpose. To this end, we introduce the spectral density $J(\omega)$ for the force-force correlation function such that the quantum dissipation term in Eq. (2.19) can be expressed as[49]

$$G_>(t)=\int d\omega\,\frac{J(\omega)}{\pi\hbar}\{[n(\omega)+1]g_-(\omega,t)+n(\omega)g_+(\omega,t)\}. \tag{2.20}$$

Here, $n(\omega)$ is the occupation number $n(\omega)=[\exp(\hbar\beta\omega)-1]^{-1}$, and the two auxiliary functions g_+ and g_- obey

$$\dot{g}_-(\omega,t)=Q\rho(t)-i\mathscr{L}_0g_-(\omega,t)-i\omega g_-(\omega,t) \tag{2.21}$$

and

$$\dot{g}_+(\omega,t)=Q\rho(t)-i\mathscr{L}_0g_+(\omega,t)+i\omega g_+(\omega,t), \tag{2.22}$$

respectively. Equation (2.17), together with Eqs. (2.20), (2.21), and (2.22), is the central result of phase-space Bloch–Redfield theory. To solve these coupled operator equations, the bath can be effectively represented by a set of harmonic oscillators weighted by the spectral density, and the quantum dissipation due to each oscillator is described by a pair of functions g_+ and g_- which are solved simultaneously with the system density matrix ρ. In this way, the quantum dissipative dynamics under colored noise (non-Markovian systems) can be transformed into coupled quantum dissipative dynamics under white noise (extended Markovian systems). As a result, the numerical techniques developed to propagate the density matrix for white noise[43] can be used to solve for the colored noise case as well.

C. Exponential decay correlation

The phase-space Bloch–Redfield theory can be simplified enormously for an exponential decay friction kernel, defined as

$$\eta(t)=\eta De^{-Dt}, \tag{2.23}$$

with D the decay rate and η the friction strength. According to the fluctuation–dissipation theorem, the classical force-force correlation function is given by

$$C(t)=kT\eta(t)=\eta kTDe^{-Dt}, \tag{2.24}$$

with k the Boltzmann constant. In the classical limit of the bath, the quantum force-force correlation function becomes

$$C_>(t)=C(t)+i\,\frac{\hbar\beta}{2}\,\dot{C}(t), \tag{2.25}$$

where the pure imaginary term is required to maintain detailed balance. This is necessary even at high temperature because of the quantum nature of the system–bath interaction. It should also be pointed out the exponential decay function is not analytical at $t=0$, giving $\dot{C}(t)=-\eta D^2kTe^{-Dt}$ and $\ddot{C}(t)=\eta D^3kTe^{-Dt}-\eta D^2kT\delta(t^+)$. Making use of these relations, the integral form in Eq. (2.19) can now be removed. With the introduction of $i\hbar g=G_>-G_<$, we have the linear operator equations

$$\dot{\rho}(t)=-i\mathscr{L}_0\rho(t)+\frac{1}{i\hbar}\,[Q,g(t)] \tag{2.26}$$

and

$$\dot{g}(t)=-i\mathscr{L}_0g(t)-Dg(t)+\frac{1}{i\hbar}\,\eta DkT[Q,\rho(t)]-\eta D^2\,\frac{1}{2}\,[Q,\rho(t)]_+, \tag{2.27}$$

with anticommutator $[A,B]_+=AB+BA$.

As pointed out earlier, the exponential decay correlation is a very special case because taking the time derivative of the exponential decay correlation function does not change the functional form of the correlation function. Due to this fact, the general Langevin equation for an exponential decay friction kernel can be transformed into a pair of coupled Langevin equations.[24,50] Similarly, the phase-space Bloch–Redfield theory, described in the last subsection for an exponential decay correlation, can be formulated as a pair of coupled quantum dissipative equations.

III. DISCUSSION

A. Fokker–Planck equation

The white noise bath can be easily recovered by taking the limit of exponential decay noise as $\lim_{D\to\infty}\eta(t)=\eta\delta(t^+)$. Without loss of generality, linear coupling is assumed, $Q=q$, implying that the dissipation is coordinate-independent. Then, the two coupled Liouville equations in Eqs. (2.26) and (2.27) can be reduced to

$$\dot{\rho}=-i\mathscr{L}_0\rho-\frac{\eta KT}{\hbar^2}[q,[q,\rho]]+\frac{1}{i\hbar}\frac{\eta}{M}\left[q,\frac{1}{2}[p,q]_+\right], \tag{3.1}$$

with M the mass and p the momentum operator. This result was first obtained by Caldeira and Leggett based on Feynman's influence functional formulation of quantum dissipation.[51]

Next, taking the classical correspondence of $[A,B]_+/2 = AB$ and $[A,B]/i\hbar=\{A,B\}$, we recover the classical Fokker–Planck equation

$$\dot{\rho}=\{H_0,\rho\}+\eta kT\frac{\partial^2}{\partial p^2}\rho+\frac{\eta}{M}\frac{\partial}{\partial p}p\rho, \tag{3.2}$$

where $\{\,,\}$ is the Poisson bracket.

As pointed out earlier, in the Markovian limit, the general Liouville equation reduces to the Bloch equation in eigenstate space. Therefore, the above derivation of the quantum Fokker–Planck equation demonstrates the accuracy of the Bloch–Redfield equation in the Markovian limit. This is not surprising because the higher order commutators ignored in Eq. (2.13) involve convolutions of force-force correlation functions which will integrate to zero if the memory time of the bath is much smaller than the time scale of the system.

For a general exponential decay noise, Eqs. (2.26) and (2.27) become Fokker–Planck-like equations in the classical limit, giving

$$\dot{\rho}=\{H_0,\rho\}+\{q,g\} \tag{3.3}$$

and

$$\dot{g}=\{H_0,g\}-Dg+\eta DkT\{q,\rho\}-\eta D^2 q\rho. \tag{3.4}$$

These two coupled partial-differential equations can be understood as the first-order generalized Fokker–Planck equations corresponding to the general Langevin equation for the exponential decay correlation.

It is well-known that the general Langevin equation with the exponential decay friction kernel can be reduced to a two-dimensional Markovian process.[50,52,53] The resulting Fokker–Planck equation has three variables, and can be transformed into an infinite series of coupled two-variable Fokker–Planck equations. Therefore, the above two equations can be viewed as the leading two equations in this series. Here, the Fokker–Planck equations are examined as the classical limit of phase-space Bloch–Redfield theory, so that classical and quantum dissipative dynamics can be treated on the same level of approximation.

B. Detailed balance

One of the basic properties of quantum correlation functions is the periodic condition[48,54]

$$C_>(t-i\hbar\beta)=C_<(t), \tag{3.5}$$

which is strikingly different from the time-reversal symmetry of classical correlation functions. In Fourier space, the above relation can be rewritten as

$$\hat{C}_>(\omega)=e^{-\beta\hbar\omega}\hat{C}_<(\omega), \tag{3.6}$$

which can be easily recognized as the detailed balance condition. As a result, even at high temperature, direct substitution of quantum correlation functions by their classical counterparts in Eq. (2.19) will violate the detailed balance of the system and thus fail to recover thermal equilibrium as the stable solution.

By imposing the detailed balance condition in Eqs. (3.5) or (3.6), we can approximate quantum correlation functions by the corresponding classical ones. One choice is to identify quantum linear response functions with their classical counterparts, and the resulting quantum correlation functions are then given by

$$\hat{C}_>(\omega)=(\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\hat{C}_{cl}(\omega), \tag{3.7}$$

which holds exactly for a harmonic bath. This approach is effectively the dispersion polaron model pioneered by Warshel.[55,56] The implication of Eq. (3.7) in the Bloch–Redfield theory has been discussed earlier by Bader and Berne.[35] It is argued by Cao and Voth[57] that replacing the classical correlation functions in Eq. (3.7) by the correlation functions obtained from classical dynamics based on the centroid potential energy surface provides a much better approximation for the quantum correlation functions.

Expanding Eq. (3.7) to first order in quantum correction, we obtain

$$\hat{C}_>(\omega)=[1+(\hbar\beta\omega/2)]\hat{C}_{cl}(\omega), \tag{3.8}$$

which is obviously the same expression as Eq. (2.25). As seen from the derivation of the quantum and classical Fokker–Planck equations in the previous subsection, the imaginary part in Eq. (2.25) gives rise to the last term in Eqs. (3.1) and (3.2), which is required to balance the diffusion term in order to achieve the thermal equilibrium. Essentially, it is the quantum nature of the bath–system interaction that requires the introduction of the imaginary part in Eq. (2.25) in order to maintain the detailed balance of the quantum system. In fact, detailed balance can be used to test the self-consistency of theories and algorithms for mixed quantum-classical systems.

C. Transformation of the bath Hamiltonian

The reduced equation of motion in Eq. (2.13) is obtained under the assumption that higher order cumulants can be ignored. This is valid if the dissipation is weak or if the correlation time of the dissipation is short, such as in the Markovian limit. If neither of these conditions is satisfied, the validity of the second-order truncation in Eq. (2.13) becomes questionable. This difficulty can be avoided if the separation of system and bath is properly partitioned so that the system–bath interaction becomes weak and noncorrelated. There are many ways to achieve this. Here we will introduce a transformation of the bath Hamiltonian to repartition system and bath.

It is well-known that the general Langevin equation is equivalent to the harmonic bath model[58] described by

$$\begin{aligned}H&=H_0(q)+H_b(x)+V_{\text{int}}(q,x)\\&=H_0(q)+\sum_{i=1}^{N}\left[\frac{m_i\dot{x}_i^2}{2}+\frac{m_i\omega_i^2}{2}\left(x_i-\frac{c_i}{m_i\omega_i^2}\,q\right)^2\right],\end{aligned}\tag{3.9}$$

where $\{m_i,\omega_i,c_i\}$ are a set of masses, frequencies, and coupling constants for the bath oscillators. The spectral density of the force-force correlation function in Eq. (2.20) is related to the harmonic bath by

$$J(\omega)=\sum_i\ \frac{\pi}{2}\,\frac{c_i^2}{m_i\omega_i}\ \delta(\omega-w_i),\tag{3.10}$$

which defines the density of states of the bath oscillators. This harmonic bath model is widely used in studying dissipative processes such as quantum tunneling and condensed phase spectroscopy.

One approach is to identify a collective bath mode, to include it in the extended system, and to treat the rest of the harmonic oscillators as the secondary bath. The system couples only to the collective bath mode, and the bath mode in turn couples to the secondary bath. Then, the composite Hamiltonian is expressed as

$$H=H_0(q)+\frac{1}{2}\,m_0\dot{x}_0^2+\frac{1}{2}\,m_0\omega_0^2\left(x_0-\frac{c_0}{m_0\omega_0^2}\,q\right)^2+H_b'(\overline{x}),\tag{3.11}$$

where the secondary bath Hamiltonian is

$$H_b'(\overline{x})=\sum_{n=1}^{N-1}\left[\frac{\overline{m}_n\dot{\overline{x}}_n^2}{2}+\frac{\overline{m}_n\overline{\omega}_n^2}{2}\left(\overline{x}_n-\frac{\overline{c}_n}{\overline{m}_n\overline{\omega}_n^2}\,x_0\right)^2\right].\tag{3.12}$$

Here, m_0, ω_0, and c_0 are the mass, frequency, and coupling constant of the collective bath mode, and $\{\overline{m}_n,\overline{\omega}_n,\overline{c}_n\}$ are a set of masses, frequencies, and coupling constants for the secondary bath oscillators. To distinguish them from the similar parameters in the harmonic bath Hamiltonian in Eq. (3.9), the parameters for the secondary bath are denoted with an overbar. By integrating out the secondary bath, the collective bath mode is effectively a Brownian oscillator.

The partitioning of the bath into the collective bath mode and the secondary bath has been proposed earlier in the context of quantum tunneling in dissipative systems.[59] In the case of electron transfer, Eq. (3.9) corresponds to the spin-boson model, where an electronic variable couples to a harmonic bath, and Eq. (3.11) corresponds to the model used by Garg *et al.*,[60] where an electronic variable couples a single nuclear coordinate, which then couples to a harmonic bath. For the accurate path integral treatment of quantum dissipation, the two Hamiltonians described here are exactly equivalent. Because of the approximate nature of the second cumulant expansion in Eq. (2.12), the partitioning of the bath can reduce the effective dissipation and thus increase the accuracy of the phase-space Bloch–Redfield equations.

The transformation between these two Hamiltonians has been established by relating the parameters of the Brownian oscillator $\{x_0,\overline{x_n}\}$ to those of the original harmonic bath $\{x_i\}$:

$$\omega_0^2=\frac{\Sigma_i c_i^2/m_i}{\Sigma c_i^2/m_i\omega_i^2},\tag{3.13}$$

$$\frac{c_0^2}{m_0}=\sum_i\ \frac{c_i^2}{m_i},\tag{3.14}$$

and an identity valid for an arbitrary variable z,

$$\sum_n\ \frac{\overline{c_n^2}}{\overline{m_i}m_0(\overline{\omega_i^2}+z)}=\omega_0^2+z-\frac{\Sigma_i c_i^2/m_i}{\Sigma_i c_i^2/m_i(\omega_i^2+z)}.\tag{3.15}$$

For derivation of these relations, see Appendix C in Ref. 59 by Caldeira and Leggett, Ref. 60 by Garg, Onuchic, and Ambegaokar, and Appendix B in Ref. 61 by Cao and Voth.

In the context of electron transfer, the collective mode alone gives rise to the classical activation energy and electron transfer rate constant.[61] Therefore, it is reasonable to view ω_0 as a characteristic frequency of the environment and to include the rest of the bath only when the dissipation and quantum effects are significant. Furthermore, it should be noted that the dissipation on the Brownian oscillator by the secondary bath is independent of the strength of the original friction kernel. Since the collective bath mode captures the major contribution to dissipation from the bath, the secondary dissipation is significantly weaker, and thereby the reduced Liouville equation in Eq. (2.13) becomes applicable.

IV. CONCLUSION

In this paper, we have formulated the Bloch–Redfield theory in phase-space and removed the Markovian approximation used in the Bloch equation. The resulting operator equations can be solved without tensor algebra and can be reduced to the Bloch equation and the Fokker–Planck equation in the proper limits. For an exponential decay correlation, the general formulation can be simplified to a pair of coupled Liouville equations. However, the second-order cumulant truncation sets the limitation of the theory to weak couplings or short correlations. In this paper, we employ a proper partitioning of the system and bath Hamiltonians, which greatly extends the applicability of the phase-space Bloch–Redfield equation. As an example, the transformation between a Gaussian bath and a Brownian oscillator is studied. In short, this composite theory represents a successful attempt toward a phase-space relaxation theory which treats classical and quantum dissipative dynamics on the same level of approximation.

For the rigor of the theory, we have to address several conceptual problems such as the positiveness of the density matrix and high order correction. The root of possible negativity of the Redfield theory is primarily the second-order cumulant truncation in deriving Eq. (2.13). However, a proper preparation of the initial bath-system configuration can significantly reduce the negative values in the Redfield theory (without the secular approximation).[28,62] There is no better way to eliminate the negative values than to include higher order cumulant expansion terms. Though such a theory would be valid for arbitrary coupling strengths and correlation times, it will be considerably more complicated and demanding to evaluate the higher order corrections.[31,63] In this sense, Bloch–Redfield theory can be viewed as the leading order in a hierarchy of coupled dissipative Liouville equations.

In a companion paper by Che and Cao,[46] the energy relaxation and dephasing processes of a Morse oscillator under exponential decay dissipation are numerically studied within this theory and compared with the classical generalized Langevin equation and the quantum master equation. Direct propagation of the reduced density matrices is carried out to solve the coupled phase-space Liouville equations. In the same paper, the approximations implied in Eq. (2.13) and the quantum properties of the exponential decay friction kernel are further discussed.

The phase-space representation of Bloch–Redfield theory provides a direct picture of the relaxation process of a photoinduced coherent wave packet. More importantly, it provides a theoretical framework for incorporating various classical and semiclassical dynamics. This is necessary because exact quantum simulations of complicated dissipative systems is intractable and the classical picture becomes more helpful. The details of mixed quantum-and-classical dissipative dynamics will be fully investigated in the future. The capability of studying large dissipative systems allows a more deterministic description of the dynamics. Applications of this version of Bloch–Redfield theory to condensed-phase spectroscopy, electron transfer, and quantum control of dissipative systems, will be interesting directions to explore.

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