ARTICLE

Evaluations on Some Perturbative Quantum Dissipation Approaches

Ying Zhang, Jin-jin Ding*, Rui-xue Xu

Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

We compare the results of some perturbative quantum dissipation approaches to the exact linear absorption of two state systems. The considered approximate methods are the so-called complete second-order quantum dissipation theories, in either the chronological ordering prescription or the correlated driving-dissipation form. Analytical results can be derived for the linear absorption of two-state systems. Assessments on their applicability are then made by comparison to the exact results.

Key words: Quantum dissipation, Perturbation theory, Absorption spectroscopy, Correlated driving-dissipation equation

I. INTRODUCTION

Dissipation is often inevitable and plays an important role in many fields of modern science [1, 2]. The fundamental interest of quantum dissipation theory (QDT) is the dynamics of a quantum system embedded in a quantum thermal bath. The key quantity is thus the reduced system density operator, *i.e.* the partial trace of total composite density matrix over the bath space. For Gaussian bath, exact formalism has been established in either the influence functional path integral [2–4] or its equivalent differential version in terms of hierarchical equations of motion [5–9]. However, exact approaches are numerically too expensive for large systems. Approximate methods are thus still needed and assessments on their applicability are required.

Perturbative approaches had been widely applied in the past. In this work, we recall the complete second-order QDTs (CS-QDTs) [10], which are rigorous up to second order of system-bath interaction with higher order contributions treated in certain re-summation ways. Two forms of CS-QDTs will be considered in this work. One is the so-called correlated driving-dissipation equations (CODDE). The other is the chronological-ordering-prescription (COP) memory-kernel CS-QDT (CS-COP-QDT). Both of them lead to linearly coupled differential equations that are convenient to calculate spectroscopic response functions [11]. For the linear absorption of a two-state system, analytical expressions can be derived. Assessments are then made by comparison to the exact results. In the remainder of work, we summarize the models and theory, and present the results and conclusions.

———————

*Author to whom correspondence should be addressed. E-mail: djjing@gmail.com

II. THEORY

A. Background of bath statistics

Let us start with the total Hamiltonian written as

$$H_{\text{Tot}}(t) = H(t) + QF_{\text{B}} + h_{\text{B}} \qquad (1)$$
$$H(t) = H_{\text{s}} + H_{\text{int}}(t) \qquad (2)$$

here, $H(t)$ is the reduced system Hamiltonian which can be time-dependent and h_{B} is the bath Hamiltonian. For simplicity, we consider only single-mode system-bath interaction with Q being a generalized system coordinate. F_{B} is the generalized Langevin force with zero mean, *i.e.*,

$$\langle F_{\text{B}} \rangle_{\text{B}} = 0 \qquad (3)$$
$$\langle \cdot \rangle_{\text{B}} \equiv \text{tr}_{\text{B}}(\cdot \rho_{\text{B}}^{eq})$$
$$\equiv \frac{\text{tr}_{\text{B}}(\cdot e^{-\beta h_{\text{B}}})}{\text{tr}_{\text{B}}(e^{-\beta h_{\text{B}}})} \qquad (4)$$

We set $\beta = 1/(k_{\text{B}}T)$ and $\hbar \equiv 1$ throughout the work.

The effect of bath is characterized by its force-force correlation function

$$C_{\text{B}}(t) \equiv \langle e^{ih_{\text{B}}t}F_{\text{B}}e^{-ih_{\text{B}}t}F_{\text{B}} \rangle_{\text{B}} \qquad (5)$$

It relates to the bath spectral density $J(\omega)$ via the fluctuation-dissipation theorem [2, 10]:

$$C_{\text{B}}(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}J(\omega)}{1 - e^{-\beta\omega}} \qquad (6)$$

In this work, we will adopt the Drude mode:

$$J(\omega) = \frac{2\lambda\gamma\omega}{\omega^2 + \gamma^2} \qquad (7)$$

where λ is the bath reorganization energy and γ indicates the spectral width. It leads to the bath correlation function to be of the following form

$$C_{\mathrm{B}}(t > 0) = c_0 \mathrm{e}^{-\gamma t} + \sum_{k=1}^{\infty} c_k \mathrm{e}^{-\gamma_k t} \qquad (8)$$

$$c_0 = \lambda \gamma \left[\cot \left(\frac{\beta \gamma}{2} \right) - i \right] \qquad (9)$$

$$c_k = \frac{8 k \pi \lambda \gamma}{(2 k \pi)^2 - (\beta \gamma)^2}, \quad k \geq 1 \qquad (10)$$

In Eq.(8), $\gamma_{k \geq 1} = 2 \kappa \pi / \beta$ are the Matsubara frequencies. In application, the infinite summation in Eq.(8) will have to be truncated up to $k \leq K$. However, it is practically exact as long as K is large enough. For later use, we denote $\gamma_0 \equiv \gamma$.

B. Model of the two-state system

The total system-plus-bath Hamiltonian under the rotating-wave-approximation assumes

$$H_{\mathrm{Tot}}(t) = H_{\mathrm{M}} + H_{\mathrm{int}}(t) \qquad (11)$$

$$H_{\mathrm{M}} = H_g |g\rangle\langle g| + H_e |e\rangle\langle e| \qquad (12)$$

$$H_{\mathrm{int}}(t) = -[D_+ E(t) \mathrm{e}^{-i\delta\omega t} + D_- E^*(t) \mathrm{e}^{i\delta\omega t}] \quad (13)$$

$$D_+ = \mu |e\rangle\langle g| \qquad (14)$$

$$D_- = \mu |g\rangle\langle e| \qquad (15)$$

here, D_+ and D_- are the transition dipole operators. $E(t)$ is the complex electric field envelop of the laser pulse and $\delta\omega = \omega - \omega_{eg}$ is the detuning frequency. We assume the dipole moment μ to be a constant. H_g and H_e are the Hamiltonians of nuclear and solvent (bath) degrees of freedom, corresponding to the system on the electronic ground $|g\rangle$ and excited $|e\rangle$ states, respectively. For the displaced-harmonic-oscillator model, they are

$$H_g = \sum_j \left[\frac{p_j^2}{2 m_j} + \frac{1}{2} m_j \omega_j{}^2 \left(x_j - \frac{c_j}{2 m_j \omega_j{}^2} \right)^2 \right] \quad (16)$$

$$H_e = \sum_j \left[\frac{p_j^2}{2 m_j} + \frac{1}{2} m_j \omega_j{}^2 \left(x_j + \frac{c_j}{2 m_j \omega_j{}^2} \right)^2 \right] \quad (17)$$

The solvation coordinate is

$$U = H_e - H_g = \sum_j c_j x_j \qquad (18)$$

and the reorganization energy is

$$\lambda = \sum_j \frac{c_j{}^2}{2 m_j \omega_j{}^2} \qquad (19)$$

Initially we assume

$$\rho_{\mathrm{Tot}} \propto \mathrm{e}^{-\beta H_g} |g\rangle\langle g| \qquad (20)$$

In terms of

$$H_{\mathrm{M}} = H_{\mathrm{s}} + Q F_{\mathrm{B}} + h_{\mathrm{B}} \qquad (21)$$

we have

$$h_{\mathrm{B}} = H_g \qquad (22)$$
$$H_{\mathrm{s}} = \lambda |e\rangle\langle e| \qquad (23)$$
$$Q = |e\rangle\langle e| \qquad (24)$$
$$F_{\mathrm{B}} = U - \lambda \qquad (25)$$

The exact linear absorption lineshape for this system is known to be

$$I_a(\omega) = \mu^2 \mathrm{Re} \int_0^{\infty} \mathrm{d}t \exp[i(\omega - \omega_{eg} - \lambda)t] \cdot$$
$$\exp\left[-\int_0^t \mathrm{d}\tau \int_0^{\tau} \mathrm{d}\tau' C_{\mathrm{B}}(\tau') \right] \qquad (26)$$

C. Correlated driving-dissipation equations

The CODDE is constructed via a variation of the complete second-order cumulant expansion QDT and reads [10, 11]:

$$\dot{\rho}(t) = -i\mathcal{L}(t)\rho(t) - \mathcal{R}_{\mathrm{s}}\rho(t) -$$
$$\{[Q, \tilde{Q}^{\mathrm{CODDE}}(t)] + H.c.\} \qquad (27)$$

$$\tilde{Q}^{\mathrm{CODDE}}(t) = -i \int_{-\infty}^{t} \mathrm{d}\tau' \int_{-\infty}^{\tau'} \mathrm{d}\tau C_{\mathrm{B}}(t - \tau) \mathcal{G}(t, \tau') \cdot$$
$$\{[\mathcal{L}_{\mathrm{int}}(\tau')\mathcal{G}_{\mathrm{s}}(\tau' - \tau)Q]\rho(\tau')\} \qquad (28)$$

$$\mathcal{R}_{\mathrm{s}}\rho(t) = [Q, \hat{Q}\rho(t) - \rho(t)\hat{Q}^{\dagger}] \qquad (29)$$

$$\hat{Q} = \hat{C}_{\mathrm{B}}(-\mathcal{L}_{\mathrm{s}})Q \qquad (30)$$

here, $\mathcal{L} \cdot = [H, \cdot]$, $\mathcal{G}$ is the Liouville-space propagation function satisfying

$$\frac{\partial \mathcal{G}(t, \tau)}{\partial t} = -i\mathcal{L}\mathcal{G}(t, \tau) \qquad (31)$$

$$\hat{C}_{\mathrm{B}}(\omega) = \int_0^{\infty} \mathrm{d}t \, \mathrm{e}^{i\omega t} C_{\mathrm{B}}(t) \qquad (32)$$

Particularly,

$$\hat{C}_{\mathrm{B}}(\omega = 0) = \frac{2\lambda}{\beta\gamma} - i\lambda \qquad (33)$$

The $\mathcal{R}_{\mathrm{s}}$-term is the field-free dissipation which determines the equilibrium state and the $\tilde{Q}^{\mathrm{CODDE}}$ term describes the correlation between driving and dissipation that is zero before field interaction.

For $C_{\mathrm{B}}(t)$ in the form of Eq.(8), we define

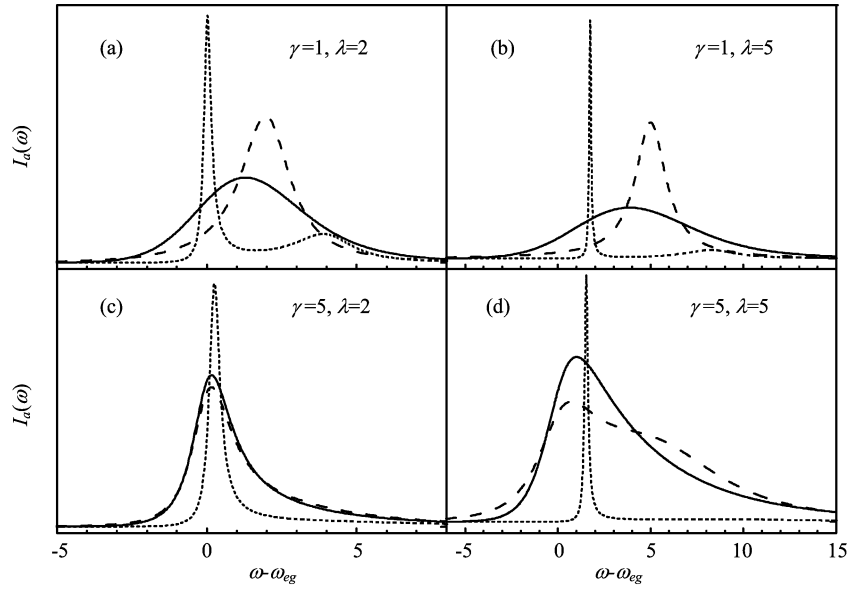$$\tilde{Q}^{\mathrm{CODDE}}(t) \equiv \sum_{k=0}^{K} c_k \tilde{Q}_k(t) \qquad (34)$$

FIG. 1 The linear absorption lineshape functions for the two-state systems at some selected values of λ and γ, evaluated by the exact expression (Eq.(26), solid curves), the CODDE (Eq.(38) and Eq.(39), dash curves) and CS-COP-QDT (Eq.(45) and Eq.(46), dot curves), respectively. The results of CS-COP-QDT are scaled with the factors 2 ((a) and (c)), 5 (b) and 10 (d).

where $\tilde{Q}_k$ is defined as in Eq.(28) according to each term in Eq.(8). The CODDE equations for the Drude bath model can then be summarized as

$$\dot{\rho}(t) = -[i\mathcal{L}(t) + \mathcal{R}_s]\rho(t) -$$
$$\sum_{k=0}^{K}[Q, c_k\tilde{Q}_k(t) - c_k^*\tilde{Q}_k^\dagger(t)] \quad (35)$$

$$\dot{\tilde{Q}}_k(t) = -[i\mathcal{L}(t) + \gamma_k]\tilde{Q}_k(t) - i[\mathcal{L}_{\text{int}}(t)\hat{Q}_k]\rho(t) \quad (36)$$

$$\hat{Q}_k = \frac{1}{\gamma_k + i\mathcal{L}_s}Q \quad (37)$$

The linear absorption calculation for the present two-state system by the CODDE approach follows the procedure in Ref.[11]. It can be obtained analytically as

$$I_a^{\text{CODDE}}(\omega) = \mu^2\text{Re}\int_0^\infty \mathrm{d}t e^{[i(\omega-\omega_{eg})t]}C_s^{\text{CODDE}}(t) \quad (38)$$

$$C_s^{\text{CODDE}}(t) = e^{-2\lambda t/(\beta\gamma)} + \sum_{k=0}^{K}\left\{\frac{c_k}{\gamma_k}\frac{e^{[-(\gamma_k+i\lambda)t]}-e^{-2\lambda t/\beta\gamma}}{[2\lambda/(\beta\gamma)]-\gamma_k-i\lambda}\right\} \quad (39)$$

D. Memory-kernel CS-COP-QDT

The CS-COP-QDT is constructed by the standard perturbation theory of quantum mechanics and obtained as [12, 13]

$$\dot{\rho}(t) = -i\mathcal{L}(t)\rho(t) - \{[Q, \tilde{Q}^{\text{COP}}(t)] + H.c.\} \quad (40)$$

$$\tilde{Q}^{\text{COP}}(t) = \int_{-\infty}^{t} \mathrm{d}\tau C_B(t-\tau)\mathcal{G}(t,\tau)[Q\rho(\tau)] \quad (41)$$

Like in the previous subsection, we introduce

$$\tilde{Q}^{\text{COP}}(t) \equiv \sum_{k=0}^{K} c_k\rho_k(t) \quad (42)$$

with ρ_k defined the same way as $\tilde{Q}^{\text{COP}}$ as in Eq.(41), corresponding to each term of $C_B(t)$ in Eq.(8). The CS-COP-QDT of Eq.(40) is now recast in the coupled equations-of-motion form as:

$$\dot{\rho}(t) = -i\mathcal{L}(t)\rho(t) - \sum_{k=0}^{K}[Q, c_k\rho_k(t) - c_k^*\rho_k^\dagger(t)] \quad (43)$$

$$\dot{\rho}_k(t) = -[i\mathcal{L}(t) + \gamma_k]\rho_k(t) + Q\rho(t) \quad (44)$$

The analytical result for the linear absorption of the two-state system can be obtained as:

$$I_a^{\text{COP}}(\omega) = \mu^2\text{Re}[F(\omega)] \quad (45)$$
$$F^{-1}(\omega) = i[\lambda - (\omega - \omega_{eg})] +$$
$$\sum_{k=0}^{K}\frac{c_k}{\gamma_k + i[\lambda - (\omega - \omega_{eg})]} \quad (46)$$

III. RESULTS

We show the absorption spectra evaluated via the approximate methods compared to the exact ones. Unit is selected to be $k_BT=1$. The typical results are demonstrated in Fig.1. The two parameters λ and γ represent, respectively, the system-bath coupling strength and Markovian/non-Markovian nature of bath.

We conclude that: (i) The CS-COP-QDT is quite unsatisfactory. It even tends to predict additional false peaks [14]; (ii) The CODDE approach is favorable with moderately small λ (weak coupling) and large γ (Markovian) parameters. This is consistent with its theoretical construction. As a perturbation theory, weak system-bath coupling should be fulfilled. Besides, it has been recognized that perturbation approaches require also the Markovian nature of bath [6]. The performance of CODDE validate its applicability in the certain range of parameters for large systems.

IV. ACKNOWLEDGMENT

[1] H. P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems*, New York: Oxford University Press, (2002).

[2] U. Weiss, *Quantum Dissipative Systems*, 3rd Edn., Singapore: World Scientific, (2008).

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

[4] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, 5th Edn., Singapore: World Scientific, (2009).

[5] Y. Tanimura and R. Kubo, J. Phys. Soc. Jpn. **58**, 101 (1989).

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

[7] A. Ishizaki and Y. Tanimura, J. Phys. Soc. Jpn. **74**, 3131 (2005).

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

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

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

[11] Y. Mo, R. X. Xu, P. Cui, and Y. J. Yan, J. Chem. Phys. **122**, 084115 (2005).

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

[13] C. Meier and D. J. Tannor, J. Chem. Phys. **111**, 3365 (1999).

[14] L. P. Chen, R. H. Zheng, Q. Shi, and Y. J. Yan, J. Chem. Phys. **131**, 094502 (2009).