Correlated driving–and–dissipation equation for non-Condon spectroscopy with the Herzberg–Teller vibronic coupling

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Correlated driving–and–dissipation equation (CODDE) is an optimized complete second–order quantum dissipation approach, which is originally concerned with the reduced system dynamics only. However, one can actually extract the hybridized bath dynamics from CODDE with the aid of dissipaton–equation–of–motion theory, a statistical quasi-particle quantum dissipation formalism. Treated as an one–dissipaton theory, CODDE is successfully extended to deal with the Herzberg– Teller vibronic couplings in dipole–field interactions. Demonstrations will be carried out on the non-Condon spectroscopies of a model dimer system.

I. INTRODUCTION

Open quantum systems are ubiquitous in most fields of modern science.¹⁻³ Quantum dissipation theory (QDT) dealing with the dynamics of open systems, such as quantum master equations, $^{4-10}$ is concerned with the reduced system dynamics. Its focus is the reduced density operator, $\rho_{\rm S}(t) \equiv {\rm tr}_{\rm B} \rho_{\rm T}(t)$, the bath subspace partial trace of the total composite density operator. As a complete second-order quantum dissipation theory (CS-QDT), the correlated driving-and-dissipation equation (CODDE) method is of high efficiency.¹¹⁻¹⁴ It is also found to be of high accuracy in its applicability range.^{15,16} On the other hand, quasi-particle descriptions for baths can provide a unified treatment on hybridized bath dynamics and entangled system-bath properties. This is right the point of the construction of the exact dissipaton-equation-ofmotion (DEOM) formalism for Gaussian baths.^{17,18} The DEOM adopts "dissipatons" as quasi-particles associated with the bath coupling statistical dynamics. For just the reduced system dynamics it recovers the hierarchical equations of motion (HEOM).^{19–27} Beside, the underlying dissipaton algebra enables DEOM an explicit theory for the hybridized bath dynamics.^{17,28–30}

The CODDE considers explicitly the drivingdissipation correlation, which makes it convenient to plug-in the quasi-particle picture for treating the hybridized bath dynamics. To observe that second-order QDTs are actually one-dissipaton theories, we have extended the CODDE to handle the Fano interference spectroscopies in previous work.³¹ However, the Herzberg-Teller vibronic couplings in dipole-field interactions are still out of reach. Theoretical study on the non-Condon vibronic coupling effect needs to deal with the hybridization between the system and the vibrational bath. By the Herzberg–Teller approximation, the bath degrees of freedom would be included in the transition dipole moments.^{32,33} In this work, we successfully extend CODDE to deal with the Herzberg-Teller vibronic couplings and simulate the corresponding non-Condon spectroscopies.

The rest of paper is organized as follows. The DEOM theory is briefly introduced in Sec. II. In Sec. III we extend CODDE to deal with the Herzberg–Teller vibronic couplings with the aid of DEOM theory. Simulations will be carried out on the non-Condon spectroscopies of a model dimer system in Sec. IV. We summarize this paper in Sec. V.

II. THE DEOM FORMALISM

A. Prelude

Let us start from the total composition Hamiltonian which assumes a form

$$H_{\rm T}(t) = H_{\rm M} - \hat{\mu}_{\rm T} \epsilon(t) \equiv H_{\rm S} + h_{\rm B} + \sum_a \hat{Q}_a^{\rm S} \hat{F}_a^{\rm B} - \hat{\mu}_{\rm T} \epsilon(t), \quad (1)$$

where the external classical field $\epsilon(t)$ polarizes both the system and bath environment. For the Herzberg–Teller coupling, we consider the total dipole moment to be

$$\hat{\mu}_{\mathrm{T}} = \hat{\mu}_{\mathrm{S}} \otimes \left(1 + \sum_{a} \hat{\mu}_{a}^{\mathrm{B}}\right) = \hat{\mu}_{\mathrm{S}} \otimes \left(1 + \sum_{a} \nu_{a}^{\mathrm{B}} \hat{F}_{a}^{\mathrm{B}}\right). \quad (2)$$

Here, $H_{\rm s}$ and $h_{\rm B} = \sum_{j} \omega_j (p_j^2 + x_j^2)$ are the Hamiltonians of an arbitrary quantum system and a harmonic bath, respectively. The system dissipative operators, $\{\hat{Q}_a^{\rm s}\}$, and dipole operators, $\hat{\mu}_{\rm s}$, are arbitrary and set to be dimensionless. The bath hybridization operators, $\{\hat{F}_a^{\rm B}\}$, are linear, i.e. $\hat{F}_a^{\rm B} = \sum_j c_j^a x_j$, and the bath dipole components, $\{\hat{\mu}_a^{\rm B}\}$, are assumed to be $\hat{\mu}_a^{\rm B} \equiv \nu_a^{\rm B} \hat{F}_a^{\rm B} = \mu_a^{\rm B} \hat{F}_a^{\rm B}/(2\lambda_a)$ where λ_a is the reorganization energy given later. Throughout this paper we set $\hbar = 1$ and $\beta = 1/(k_B T)$ with $k_{\rm B}$ being the Boltzmann constant and T the temperature.

The effects of such a Gaussian bath are characterized by the bath coupling correlation functions,

$$C_{ab}(t) \equiv \langle \hat{F}_{a}^{\mathrm{B}}(t) \hat{F}_{b}^{\mathrm{B}}(0) \rangle_{\mathrm{B}}$$

$$\equiv \mathrm{tr}_{\mathrm{B}} \left(e^{ih_{\mathrm{B}}t} \hat{F}_{a}^{\mathrm{B}} e^{-ih_{\mathrm{B}}t} \hat{F}_{b}^{\mathrm{B}} e^{-\beta h_{\mathrm{B}}} \right) / \mathrm{tr}_{\mathrm{B}} e^{-\beta h_{\mathrm{B}}}. \quad (3)$$

They are related with the bath coupling spectral densities,

$$J_{ab}(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}t \, e^{i\omega t} \langle [\hat{F}_{a}^{\mathrm{B}}(t), \hat{F}_{b}^{\mathrm{B}}(0)] \rangle_{\mathrm{B}} = J_{ba}^{*}(\omega) \,, \quad (4)$$

via the fluctuation–dissipation theorem as:^{1,13}

$$C_{ab}(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \, \frac{e^{-i\omega t} J_{ab}(\omega)}{1 - e^{-\beta\omega}} \,. \tag{5}$$

The associated bath reorganization energy is¹

$$\lambda_a = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{J_a(\omega)}{\omega} \,. \tag{6}$$

To impose the quasi-particles on bath influences, exponential expansions of bath correlations are needed, i.e.

$$C_{ab}(t) = \sum_{k=1}^{K} \eta_{abk} e^{-\gamma_k t}.$$
(7)

The coefficients in the exponents, $\{\gamma_k\}$, required by Eq. (5), should be either real or complex conjugate paired. Defining $\gamma_{\bar{k}} \equiv \gamma_k^*$, there would be

$$C_{ab}(-t) = C_{ba}^{*}(t) = \sum_{k=1}^{K} \eta_{abk}^{*} e^{-\gamma_{k}^{*}t} = \sum_{k=1}^{K} \eta_{ab\bar{k}}^{*} e^{-\gamma_{k}t}.$$
 (8)

The following quasi-particle descriptions on baths are just introduced on basis of Eq. (7) with the property of Eq. (8). Here, we assume $\{\gamma_k\}$ independent of a, b. Extension to general cases is straightforward.^{25,30}

B. The dissipaton algebra

The DEOM construction starts from the dissipaton decomposition on the hybridization bath operator, ^{17,28}

$$\hat{F}_a^{\mathsf{B}} = \sum_{k=1}^{K} \hat{f}_{ak},\tag{9}$$

where the involving statistically independent dissipatons satisfy

$$\langle \hat{f}_{ak}(t)\hat{f}_{bj}(0)\rangle_{\rm B} = \delta_{kj}\eta_{abk}e^{-\gamma_k t}, \langle \hat{f}_{bj}(0)\hat{f}_{ak}(t)\rangle_{\rm B} = \delta_{kj}\eta^*_{ab\bar{k}}e^{-\gamma_k t},$$
 (10)

to reproduce Eqs. (7) and (8). It thus leads to the generalized diffusion equation of dissipatons, 17,28

$$\operatorname{tr}_{\mathrm{B}}\left[\left(\frac{\partial}{\partial t}\hat{f}_{ak}\right)_{\mathrm{B}}\rho_{\mathrm{T}}(t)\right] = -\gamma_{k}\operatorname{tr}_{\mathrm{B}}\left[\hat{f}_{ak}\rho_{\mathrm{T}}(t)\right],\qquad(11)$$

where

$$\left(\frac{\partial}{\partial t}\hat{f}_{ak}\right)_{\rm B} = -i[\hat{f}_{ak}, h_{\rm B}],\tag{12}$$

obeys the Heisenberg equation of motion in bare bath.

The dissipaton density operators (DDOs) that constitute the DEOM are defined as: 17,28

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \operatorname{tr}_{\mathrm{B}}\Big[\Big(\prod_{ak} \hat{f}_{ak}^{n_{ak}}\Big)^{\circ} \rho_{\mathrm{T}}(t)\Big].$$
(13)

Here, $\mathbf{n} = \{n_{ak}\}, n = \sum_{ak} n_{ak}$, and $(\cdots)^{\circ}$ denotes the *irreducible* product. For bosonic dissipatons, $(\hat{f}_{ak}\hat{f}_{bj})^{\circ} = (\hat{f}_{bj}\hat{f}_{ak})^{\circ}$, and $n_{ak} = 0, 1, \cdots$ can be viewed as the occupation numbers of individual dissipatons. For the later

construction of DEOM, denote also $\rho_{\mathbf{n}_{ak}}^{(n\pm 1)}$ as the associated $(n\pm 1)$ -DDOs, with \mathbf{n}_{ak}^{\pm} differing from **n** only at the specified \hat{f}_{ak} -disspaton occupation number, n_{ak} , by ± 1 . The involving generalized Wick's theorem on dissipatons thus reads,^{17,28} cf. Eq. (10),

$$\operatorname{tr}_{\mathrm{B}} \left[\left(\prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} \hat{f}_{bj} \rho_{\mathrm{T}}(t) \right]$$

= $\rho_{\mathbf{n}_{bj}^{+}}^{(n+1)}(t) + \sum_{ak} n_{ak} \langle \hat{f}_{ak}(0^{+}) \hat{f}_{bj}(0) \rangle_{\mathrm{B}} \rho_{\mathbf{n}_{ak}^{-}}^{(n-1)}(t), \quad (14)$

and

$$\operatorname{tr}_{B} \left[\left(\prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} \rho_{\mathrm{T}}(t) \hat{f}_{bj} \right]$$

= $\rho_{\mathbf{n}_{bj}^{+}}^{(n+1)}(t) + \sum_{ak} n_{ak} \langle \hat{f}_{bj}(0) \hat{f}_{ak}(0^{+}) \rangle_{B} \rho_{\mathbf{n}_{ak}^{-}}^{(n-1)}(t).$ (15)

These dissipaton algebra will be used in the later DEOM construction in the presence of non-Condon external field excitation.

C. The DEOM construction

The DEOM can now be readily constructed by applying $\dot{\rho}_{\rm T}(t) = -i[H_{\rm T}(t), \rho_{\rm T}(t)]$, to the total composite density operator in Eq. (13); i.e.,

$$\dot{\rho}_{\mathbf{n}}^{(n)}(t) = -i \operatorname{tr}_{\mathrm{B}} \left\{ \left(\prod_{ak} \hat{f}_{ak}^{n_{ak}} \right)^{\circ} [H_{\mathrm{T}}(t), \rho_{\mathrm{T}}(t)] \right\}.$$
(16)

By Eq. (11) with Eq. (12) and Eqs. (14)-(15), the final DEOM formalism, with the total Hamiltonian given in Eq. (1), is resulted as

$$\dot{\rho}_{\mathbf{n}}^{(n)} = -\left[i\mathcal{L}(t) + \sum_{ak} n_{ak}\gamma_k\right]\rho_{\mathbf{n}}^{(n)} - i\sum_{ak} \left[\mathcal{A}_a - \mathcal{D}_a\epsilon(t)\right]\rho_{\mathbf{n}_{ak}^+}^{(n+1)} - i\sum_{ak} n_{ak} \left[\mathcal{C}_{ak} - \mathcal{D}'_{ak}\epsilon(t)\right]\rho_{\mathbf{n}_{ak}^-}^{(n-1)}.$$
(17)

Here,

$$\mathcal{L}(t)\hat{O} \equiv [H_{\rm s} - \hat{\mu}^{\rm s} \epsilon(t), \hat{O}], \qquad (18a)$$

$$\mathcal{A}_{a}\hat{O} \equiv [\hat{Q}_{a}^{\mathrm{s}}, \hat{O}], \qquad \mathcal{D}_{a}\hat{O} \equiv \nu_{a}^{\mathrm{B}}[\hat{\mu}_{\mathrm{s}}, \hat{O}], \qquad (18\mathrm{b})$$

$$\mathcal{C}_{ak}\hat{O} \equiv \sum_{b} \left(\eta_{abk} \hat{Q}_{a}^{\mathrm{s}} \hat{O} - \eta_{ab\bar{k}}^{*} \hat{O} \hat{Q}_{a}^{\mathrm{s}} \right), \tag{18c}$$

$$\mathcal{D}'_{ak}\hat{O} \equiv \sum_{b} \nu_{b}^{\scriptscriptstyle B} \left(\eta_{abk} \hat{\mu}_{\scriptscriptstyle S} \hat{O} - \eta^{*}_{ab\bar{k}} \hat{O} \hat{\mu}_{\scriptscriptstyle S} \right).$$
(18d)

Therefore, the DEOM provides a unified approach to study the system–bath entangled polarizations.

D. Spectroscopies

Let us first consider the non-Condon polarization,

$$P_{\mathrm{T}}(t) = \mathrm{Tr}[\hat{\mu}_{\mathrm{T}}\rho_{\mathrm{T}}(t)] = \mathrm{tr}_{\mathrm{s}}\mathrm{tr}_{\mathrm{B}}\Big[\hat{\mu}_{\mathrm{S}}\Big(1 + \sum_{a}\hat{\mu}_{a}^{\mathrm{B}}\Big)\rho_{\mathrm{T}}(t)\Big].$$
(19)

Applying Eqs. (13) and (14), the DEOM–evaluation on it reads^{30,33}

$$P_{\rm T}(t) = {\rm tr}_{\rm s} \Big[\hat{\mu}_{\rm s} \rho^{(0)}(t) + \sum_{ak} \nu_a^{\rm B} \hat{\mu}_{\rm s} \rho_{ak}^{(1)}(t) \Big].$$
(20)

The dipole–dipole correlation function is³⁴

$$\langle \hat{\mu}_{\mathrm{T}}(t)\hat{\mu}_{\mathrm{T}}(0)\rangle \equiv \mathrm{Tr}(\hat{\mu}_{\mathrm{T}}e^{-i\mathcal{L}_{\mathrm{M}}t}\hat{\mu}_{\mathrm{T}}\rho_{\mathrm{T}}^{\mathrm{eq}}).$$
 (21)

Here, $\mathcal{L}_{\rm M} \cdot \equiv [H_{\rm M}, \cdot]$ and $\rho_{\rm T}^{\rm eq} = e^{-\beta H_{\rm M}}/\text{Tr}e^{-\beta H_{\rm M}}$ are the total matter Liouvillian and the thermal equilibrium density operator in the absence of external field, respectively [cf. Eq. (1)]. The DEOM correspondence to $\rho_{\rm T}^{\rm eq}$ is just $\rho_{\rm eq} \equiv \{\rho_{\rm n;eq}^{(n)}\}$, the steady–state solutions to the field–free DEOM (17). The DEOM evaluation on the dipole correlation function, Eq. (21), is as follows.^{29,30}

(i) Start with the aforementioned correspondence of $\rho_{\rm T}^{\rm eq} \Rightarrow \{\rho_{\rm n;eq}^{(n)}\}$, by evaluating the steady-state solutions to the field-free Eq. (17);

(ii) Identify $\hat{\mu}_{\rm T} \rho_{\rm T}^{\rm eq} \Rightarrow \{ \rho_{\rm n}^{(n)}(t=0;\hat{\mu}_{\rm T}) \}$ by using Eq. (13), and obtain¹⁸

$$\rho_{\mathbf{n}}^{(n)}(t=0;\hat{\mu}_{\mathrm{T}}) \equiv \mathrm{tr}_{\mathrm{B}} \Big[\Big(\prod_{ak} \hat{f}_{ak}^{n_{ak}} \Big)^{\circ} \big(\hat{\mu}_{\mathrm{T}} \rho_{\mathrm{T}}^{\mathrm{eq}} \big) \Big] \\ = \hat{\mu}_{\mathrm{S}} \Big[\rho_{\mathbf{n};\mathrm{eq}}^{(n)} + \sum_{ak} \nu_{a}^{\mathrm{B}} \rho_{\mathbf{n}_{ak}^{+};\mathrm{eq}}^{(n+1)} + \sum_{ak,b} \nu_{b}^{\mathrm{B}} n_{ak} \eta_{abk} \rho_{\mathbf{n}_{ak}^{-};\mathrm{eq}}^{(n-1)} \Big].$$
(22)

The second identity is obtained by using Eq. (2) for $\hat{\mu}_{\rm T}$, followed by the generalized Wick's theorem, Eq. (14); (iii) The field-free DEOM propagation is then carried out to obtain $\{\rho_{\mathbf{n}}^{(n)}(t;\hat{\mu}_{\rm T})\}$, the DEOM-space correspondence to $e^{-i\mathcal{L}_{\rm M}t}(\hat{\mu}_{\rm T}\rho_{\rm T}^{\rm eq})$;

(iv) Calculate Eq. (21) in terms of the expectation value like Eq. (20); i.e.,

$$\langle \hat{\mu}_{\rm T}(t)\hat{\mu}_{\rm T}(0)\rangle = {\rm tr}_{\rm s} \Big[\hat{\mu}_{\rm s}\rho^{(0)}(t;\hat{\mu}_{\rm T}) + \sum_{ak}\nu_{a}^{\rm B}\hat{\mu}_{\rm s}\rho^{(1)}_{ak}(t;\hat{\mu}_{\rm T})\Big].$$
(23)

Note that these formulas are similar but different from that in Ref. 31 due to the different forms of total dipole.

III. THE CODDE FORMALISM

A. Prelude

The second–order perturbative approach can be viewed as one–dissipaton theories, but differ at their resummation treatments on $\{\rho_{\mathbf{n}}^{(n>1)}(t)\}$, the higher–order influence. To be concrete, the DEOM (17) with n = 0 can be recast as

$$\dot{\rho}_{\mathrm{s}}(t) = -i\mathcal{L}(t)\rho_{\mathrm{s}}(t) - i\sum_{ak} \left[\hat{Q}_{a}^{\mathrm{s}} - \nu_{a}\hat{\mu}_{\mathrm{s}}\epsilon(t), \rho_{ak}^{(1)}(t)\right].$$
(24)

The time–nonlocal formalism, also called the chronological ordering prescription (COP) of CS-QDT,^{10–13} adopts the simplest one–dissipaton level truncation by setting all $\rho_{\mathbf{n}}^{(n>1)}(t) = 0$. The resultant DEOM (17), with setting $\{\rho_{\mathbf{n}}^{(n>L)} = 0\}$ at the L = 1 level, is terminated by

$$\dot{\rho}_{ak}^{(1)}(t) \approx -\left[i\mathcal{L}(t) + \gamma_k\right]\rho_{ak}^{(1)}(t) - i[\mathcal{C}_{ak} - \mathcal{D}'_{ak}\epsilon(t)]\rho_{\rm s}(t).$$
(25)

Its formal solution is

$$\rho_{ak}^{(1)}(t) = \rho_{ak}^{\text{COP}}(t) + \delta \rho_{ak}^{\text{COP}}(t), \qquad (26)$$

with

$$\rho_{ak}^{\text{COP}}(t) = -i \int_{-\infty}^{t} \mathrm{d}\tau e^{-\gamma_k(t-\tau)} \mathcal{G}(t,\tau) \mathcal{C}_{ak} \rho_{\text{S}}(\tau), \qquad (27)$$

$$\delta \rho_{ak}^{\text{COP}}(t) = i \int_{-\infty}^{t} \mathrm{d}\tau e^{-\gamma_k(t-\tau)} \mathcal{G}(t,\tau) \mathcal{D}'_{ak} \rho_{\text{S}}(\tau) \epsilon(\tau). \quad (28)$$

Here, $\mathcal{G}(t,\tau)$ is the bath-free propagator, satisfying

$$\frac{\partial}{\partial t}\mathcal{G}(t,\tau) = -i\mathcal{L}(t)\mathcal{G}(t,\tau), \text{ with } \mathcal{G}(t,t) = 1.$$
 (29)

The time–local CS-QDT is also called the partial ordering prescription (POP) formalism.^{10–13} Within the complete second–order theory, the POP adopts the bath–free approximant of $\rho_{\rm S}(\tau) \approx \mathcal{G}(\tau,t)\rho_{\rm S}(t)$ to Eq. (27). It is noticed that $\mathcal{G}(t,\tau)\hat{O} = G(t,\tau)\hat{O}G^{\dagger}(t,\tau)$, where $G(t,\tau)$ is the Hilbert–space counterpart to $\mathcal{G}(t,\tau)$. Consequently, $\mathcal{G}(t,\tau)\{\hat{O}[\mathcal{G}(\tau,t)\rho_{\rm S}(t)]\} = [\mathcal{G}(t,\tau)\hat{O}]\rho_{\rm S}(t)$. The POP or time–local counterparts to Eq. (27) is then

$$\rho_{ak}^{\text{POP}}(t) = -i \big[\hat{X}_{ak}(t) \rho_{\text{S}}(t) - \rho_{\text{S}}(t) \hat{X}_{a\bar{k}}^{\dagger}(t) \big], \qquad (30)$$

where

$$\hat{X}_{ak}(t) = \sum_{b} \eta_{abk} \int_{-\infty}^{t} \mathrm{d}\tau e^{-\gamma_k(t-\tau)} \mathcal{G}(t,\tau) \hat{Q}_b^{\mathrm{s}}.$$
 (31)

The associated index \bar{k} , the same as that in Eq. (8), is defined via $\gamma_{\bar{k}} \equiv \gamma_{k}^{*}$. By applying the Dyson equation for the bath-free propagator, with $\mathcal{L}(t) \equiv \mathcal{L}_{s} + \mathcal{L}_{sf}(t)$,

$$\mathcal{G}(t,\tau) = \mathcal{G}_{\mathrm{s}}(t-\tau) - i \int_{\tau}^{t} \mathrm{d}\tau' \mathcal{G}(t,\tau') \mathcal{L}_{\mathrm{sf}}(\tau') \mathcal{G}_{\mathrm{s}}(\tau'-\tau).$$
(32)

This leads to Eq. (31) the expression,

$$\hat{X}_{ak}(t) = \tilde{X}_{ak} + \delta \hat{X}_{ak}(t), \qquad (33)$$

with

$$\widetilde{X}_{ak} = \sum_{b} \frac{\eta_{abk}}{i\mathcal{L}_{s} + \gamma_{k}} \hat{Q}_{b}^{s}.$$
(34)

The field-driven term, $\delta \hat{X}_{ak}(t)$, satisfies

$$\delta \dot{X}_{ak}(t) = -[i\mathcal{L}(t) + \gamma_k] \delta \dot{X}_{ak}(t) - i\mathcal{L}_{\rm sf}(t) \widetilde{X}_{ak}.$$
 (35)

Note that $\mathcal{L}_{\rm sf}(t)\hat{O} \equiv -\epsilon(t)[\hat{\mu}_{\rm s},\hat{O}].$

B. CODDE formalism

The CODDE are based on the following two ansatz. Firstly, we set $\rho_{ak}^{(1)}(t) = \rho_{ak}^{\text{POP}}(t) + \delta \rho_{ak}^{\text{COP}}(t)$ [cf. Eqs. (30) and (28)]. The CODDE correspondence to Eq. (26), as inferred from Eqs. (30) and (33), would read

$$\rho_{ak}^{(1)}(t) = -i \left[\widetilde{X}_{ak} \rho_{\mathrm{S}}(t) - \rho_{\mathrm{S}}(t) \widetilde{X}_{a\bar{k}}^{\dagger} \right] + \varrho_{ak}(t) \qquad (36)$$

where $\rho_{ak}(t)$ is defined later; see Eq. (38).

Secondly, we treats $\delta \dot{X}_{ak}(t)\rho_{\rm s}(t)$ with the second-order level linearization ansatz,

$$\frac{\mathrm{d}}{\mathrm{d}t} [\delta \hat{X}_{ak}(t) \rho_{\mathrm{S}}(t)] \approx \delta \dot{\hat{X}}_{ak}(t) \rho_{\mathrm{S}}(t) - i\delta \hat{X}_{ak}(t) [\mathcal{L}(t) \rho_{\mathrm{S}}(t)].$$

Together with Eq. (35), followed by using the commutator identity, $A(\mathcal{L}B) = \mathcal{L}(AB) - (\mathcal{L}A)B$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} \left[\delta \hat{X}_{ak}(t) \rho_{\mathrm{s}}(t) \right] \approx - \left[i \mathcal{L}(t) + \gamma_{k} \right] \left[\delta \hat{X}_{ak}(t) \rho_{\mathrm{s}}(t) \right] - i \left[\mathcal{L}_{\mathrm{sf}}(t) \widetilde{X}_{ak} \right] \rho_{\mathrm{s}}(t), \qquad (37a) \frac{\mathrm{d}}{\mathrm{d}t} \left[\rho_{\mathrm{s}}(t) \delta \hat{X}_{a\bar{k}}^{\dagger}(t) \right] \approx - \left[i \mathcal{L}(t) + \gamma_{k} \right] \left[\rho_{\mathrm{s}}(t) \delta \hat{X}_{a\bar{k}}^{\dagger}(t) \right] - i \rho_{\mathrm{s}}(t) \left[\mathcal{L}_{\mathrm{sf}}(t) \widetilde{X}_{a\bar{k}}^{\dagger} \right]. \qquad (37b)$$

Define now

$$\varrho_{ak}(t) \equiv -i \left[\delta \hat{X}_{ak}(t) \rho_{\rm S}(t) - \rho_{\rm S}(t) \delta \hat{X}^{\dagger}_{a\bar{k}}(t) \right] + \delta \rho_{ak}^{\rm COP}(t),$$
(38)

where $\delta \rho_{ak}^{\text{COP}}(t)$ of Eq. (28) satisfies

$$\delta \dot{\rho}_{ak}^{\text{COP}}(t) = -[i\mathcal{L}(t) + \gamma_k] \delta \rho_{ak}^{\text{COP}}(t) + i\epsilon(t) \mathcal{D}'_{ak} \rho_{\text{S}}(t).$$
(39)

The equation of motion for $\rho_{ak}(t)$, Eq. (38), can be completed, with its first term to be evaluated via the CODDE ansatz, Eqs. (37a) and (37b).

Finally, the CODDE formalism reads

$$\dot{\rho}_{\rm s} = -\left[i\mathcal{L}(t) + \mathcal{R}_{\rm s}(t)\right]\rho_{\rm s} - i\sum_{ak} \left[\mathcal{A}_a - \mathcal{D}_a\epsilon(t)\right]\varrho_{ak},$$
(40a)

$$\dot{\varrho}_{ak} = -\left[i\mathcal{L}(t) + \gamma_k\right]\varrho_{ak} - i\epsilon(t)(\widetilde{\mathcal{C}}_{ak} - \mathcal{D}'_{ak})\rho_{\rm S},\qquad(40\mathrm{b})$$

with

$$\mathcal{R}_{\rm S}(t)\hat{O} \equiv \sum_{ak} \left[\hat{Q}_a^{\rm s} - \epsilon(t)\nu_a^{\rm B}\hat{\mu}_{\rm S}, \widetilde{X}_{ak}\hat{O} - \hat{O}\widetilde{X}_{a\bar{k}}^{\dagger}\right], \quad (41)$$

and

$$\widetilde{\mathcal{C}}_{ak}\hat{O} \equiv i \big[\hat{\mu}_{\rm S}, \widetilde{X}_{ak}\big]\hat{O} - i\hat{O}\big[\hat{\mu}_{\rm S}, \widetilde{X}^{\dagger}_{a\bar{k}}\big].$$
(42)

The above formalism depends locally on the external field $\epsilon(t)$. In the absence of external field, $\varrho_{ak}^{eq} = \varrho_{ak}(t \rightarrow \pm \infty) = 0$ and CODDE is identical to POP formalism, Eqs. (30)–(35). However, CODDE fixes the drawback of nonlinearity, Eq. (30) with Eq. (35), for the field–dressed dissipation. On the other hand, it is well known that COP induces spurious resonances.^{10,14,35} Overall speaking, CODDE is best among aforementioned three CS-QDTs, with similar computational cost as COP.

C. Spectroscopies

Consider the polarization, $P_{\rm T}(t) \equiv {\rm Tr}[\hat{\mu}_{\rm T}\rho_{\rm T}(t)]$, on the basis of the dissipaton result, Eq. (20). Together with the CODDE's one-dissipaton quantities of Eq. (36), we obtain

$$P_{\rm T}(t) = {\rm tr}_{\rm s} \Big[\hat{\mu}_{\rm s}^{\rm eff} \rho_{\rm s}(t) + \sum_{ak} \nu_a^{\rm B} \hat{\mu}_{\rm s} \varrho_{ak}(t) \Big], \qquad (43)$$

where

$$\hat{\mu}_{\rm s}^{\rm eff} \equiv \hat{\mu}_{\rm s} \Big[1 - i \sum_{ak} \nu_a^{\rm B} \big(\widetilde{X}_{ak} - \widetilde{X}_{a\bar{k}}^{\dagger} \big) \Big]. \tag{44}$$

Turn now to the CODDE evaluation on $\langle \hat{\mu}_{T}(t)\hat{\mu}_{T}(0)\rangle$ of Eq. (21). According to Eq. (43), we have that

$$\langle \hat{\mu}_{\mathrm{T}}(t)\hat{\mu}_{\mathrm{T}}(0)\rangle = \mathrm{tr}_{\mathrm{s}}\Big[\hat{\mu}_{\mathrm{s}}^{\mathrm{eff}}\rho_{\mathrm{s}}(t;\hat{\mu}_{\mathrm{T}}) + \sum_{ak}\nu_{a}^{\mathrm{B}}\varrho_{ak}(t;\hat{\mu}_{\mathrm{T}})\Big].$$
(45)

Here, $\rho_{\rm S}(t; \hat{\mu}_{\rm T})$ and $\{\varrho_{ak}(t; \hat{\mu}_{\rm T})\}$ arise from the field-free CODDE propagation. The initial conditions are

$$\begin{bmatrix} \rho_{\rm S}(0;\hat{\mu}_{\rm T})\\ \varrho_{ak}(0;\hat{\mu}_{\rm T}) \end{bmatrix} = \begin{bmatrix} \hat{\mu}_{\rm S} + \mathcal{X}_{\rm S} & \nu_a^{\rm B}\hat{\mu}_{\rm S}\\ -\hat{W}_{ak} & \hat{\mu}_{\rm S} \end{bmatrix} \begin{bmatrix} \rho_{\rm S}^{\rm eq}\\ \rho_{ak}^{\rm eq}\\ \varrho_{ak}^{\rm eq} \end{bmatrix}.$$
(46)

where the superoperator \mathcal{X}_{s} denotes the forward (left) action component of $i\mathcal{R}_{s}(t)$ in Eq. (40),

$$\mathcal{X}_{\rm s}\hat{O} = -i\nu_a^{\rm B}\hat{\mu}_{\rm s}(\widetilde{X}_{ak}\hat{O} - \hat{O}\widetilde{X}_{a\bar{k}}^{\dagger}). \tag{47}$$

This is in line with the left and right action of Hamiltonian. Similarly, the operator \hat{W}_{ak} arises from the forward (left) action component of $(\tilde{C}_{ak} - \mathcal{D}'_{ak})$ in Eq. (40). As inferred from Eqs. (42) and (18d), we obtain

$$\hat{W}_{ak} = i \big[\hat{\mu}_{\mathrm{S}}, \widetilde{X}_{ak} \big] - \sum_{b} \nu_{b}^{\mathrm{B}} \eta_{ak} \hat{\mu}_{\mathrm{S}}.$$
(48)

This thus completes the CODDE for the non-Condon spectroscopy with the Herzberg–Teller vibronic coupling.

IV. NUMERICAL DEMONSTRATION

Consider an excitonic dimer system,

$$H_{\rm S} = \sum_{a=1}^{2} \varepsilon_a \hat{B}_a^{\dagger} \hat{B}_a + V(\hat{B}_1^{\dagger} \hat{B}_2 + \hat{B}_2^{\dagger} \hat{B}_1) + U \hat{B}_1^{\dagger} \hat{B}_1 \hat{B}_2^{\dagger} \hat{B}_2,$$
(49)

where $\hat{B}_a \equiv |0\rangle\langle a|$ $(\hat{B}_a^{\dagger} \equiv |a\rangle\langle 0|)$ are the excitonic annihilation (creation) operators. $\{\varepsilon_a\}$, V, and U are the on-site energies, the interstate coupling, and the exciton Coulomb interaction. The excitonic system is coupled to the harmonic bath via

$$H_{\rm SB} = \sum_{a=1}^{2} \hat{B}_{a}^{\dagger} \hat{B}_{a} \hat{F}_{a}^{\rm B}.$$
 (50)



FIG. 1: Linear absorption spectra $S(\omega)$ calculated by Eq. (53) in the underdamped BO case ($\zeta = V$) for various values of $\mu_{\rm B}/\mu_{\rm S}$. Left panel: $\lambda = 0.1V$; Right panel: $\lambda = 0.5V$.

The bath spectral density assumes the Brownian oscillator (BO) form

$$J_{11}(\omega) = J_{22}(\omega) = \frac{2\lambda\zeta\Omega^{2}\omega}{(\omega^{2} - \Omega^{2})^{2} - \zeta^{2}\omega^{2}},$$
 (51)

and the off-diagonal fluctuations are neglected, i.e., $J_{12} = J_{21} = 0$. The total system and bath dipole operator takes the form of Eq. (2), where the system dipole operator $\hat{\mu}_{s}$ reads

$$\hat{\mu}_{\rm s} = \mu_{\rm s} \sum_{a} (\hat{B}_a^{\dagger} + \hat{B}_a), \tag{52}$$

and the bath part is $\hat{\mu}_a^{\rm B} = \mu_{\rm B} \hat{F}_a^{\rm B}/(2\lambda)$. Here, $\mu_{\rm S}$ and $\mu_{\rm B}$ are the system and bath dipole strengths, respectively. We take V as the reference unit of energy, and set $k_B T = \varepsilon_1 = \varepsilon_2 = U = V$. The BO parameters are given as $\Omega = V, \lambda = 0.1V$ and $0.5V, \zeta = V$ (underdamped) and 4V (overdamped) for comparison.

The linear absorption spectra of the total matter are obtained via

$$S(\omega) = \operatorname{Re} \int_0^\infty dt \, e^{i\omega t} \langle \hat{\mu}_{\mathrm{T}}(t) \hat{\mu}_{\mathrm{T}}(0) \rangle.$$
 (53)

In Fig. 1, we present the linear absorption spectra in the underdamped BO case ($\zeta = V$). As the bath optical activity is switched on and tuned up, $\mu_{\rm B}/\mu_{\rm S}$ varies from -2 to 2. The results of the weak coupling case ($\lambda = 0.1V$) are exhibited in the left panel, where both COP and CODDE results are close to exact ones. The exact results are obtained from the converged DEOM calculations. In the right panel, we adopt $\lambda = 0.5V$ for the strong vibronic coupling. COP qualitatively deviates from the



FIG. 2: Linear absorption spectra $S(\omega)$ calculated by Eq. (53) in the overdamped BO case ($\zeta = 4V$) for various values of $\mu_{\rm B}/\mu_{\rm S}$. Left panel: $\lambda = 0.1V$; Right panel: $\lambda = 0.5V$.

exact ones, exhibiting spurious peaks. It is found that CODDE always behaves much better than COP.

Moreover, Fig. 2 exhibits the linear absorption spectra in the overdamped BO case ($\zeta = 4V$). We observe that even in the weak coupling case (left panel), COP is ill-behaved. CODDE would be the choice of CS-QDT, although it quantitatively deviate from the exact ones obtained via DEOM when the coupling is strong.

V. SUMMARY

In summary, we extend the CODDE, an optimized CS-QDT, to deal with the Herzberg–Teller vibronic couplings in dipole–field interactions, with the aid of DEOM formalism. As CODDE is formally an one–dissipaton theory, we can extract not only the reduced system dynamics but also the hybridized bath informations. The present theory can be readily extended to the nonequilibrium setups with multiple coupling environment baths. The heat transport current and noise spectra can also be evaluated.

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- ¹ U. Weiss, *Quantum Dissipative Systems*, World Scientific, Singapore, 2021, 5th ed.
- ² H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, World Scientific, Singapore, 5th edition, 2009.
- ³ H. P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems*, Oxford University Press, New York, 2002.
- ⁴ S. Nakajima, "On quantum theory of transport phenomena – Steady diffusion," Prog. Theor. Phys. **20**, 948 (1958).
- ⁵ R. Zwanzig, "Ensemble method in the theory of irreversibility," J. Chem. Phys. **33**, 1338 (1960).
- ⁶ H. Mori, "Transport, collective motion, and Brownian motion," Prog. Theor. Phys. **33**, 423 (1965).
- ⁷ A. G. Redfield, "The theory of relaxation processes," Adv. Magn. Reson. 1, 1 (1965).
- ⁸ G. Lindblad, "On the generators of quantum dynamical semigroups," Commun. Math. Phys. 48, 119 (1976).
- ⁹ T. O. Cheche, M. Hayashi, and S. H. Lin, "Generalised Master Equation for the Spin-Boson Hamiltonian by the Projection Operator Technique," J. Chin. Chem. Soc. 47, 729 (2000).
- ¹⁰ S. Mukamel, "Reduced equations of motion for collisionless molecular multiphoton processes," Adv. Chem. Phys. 47, 509 (1981).
- ¹¹ R. X. Xu and Y. J. Yan, "Theory of open quantum systems," J. Chem. Phys. **116**, 9196 (2002).
- ¹² R. X. Xu, Y. Mo, P. Cui, S. H. Lin, and Y. J. Yan, "Non-Markovian quantum dissipation in the presence of external fields," *Progress in Theoretical Chemistry and Physics*, *Vol. 12: Advanced Topics in Theoretical Chemical Physics*, edited by J. Maruani, R. Lefebvre, and E. Brändas, pages 7–40, Kluwer, Dordrecht, 2003.
- ¹³ Y. J. Yan and R. X. Xu, "Quantum mechanics of dissipative systems," Annu. Rev. Phys. Chem. 56, 187 (2005).
- ¹⁴ Y. Mo, R. X. Xu, P. Cui, and Y. J. Yan, "Correlation and response functions with non-Markovian dissipation: A reduced Liouville-space theory," J. Chem. Phys. **122**, 084115 (2005).
- ¹⁵ R. X. Xu, Y. J. Yan, Y. Ohtsuki, Y. Fujimura, and H. Rabitz, "Optimal control of quantum non-Markovian dissipation: Reduced Liouville-space theory," J. Chem. Phys. **120**, 6600 (2004).
- ¹⁶ J. Xu, H. D. Zhang, R. X. Xu, and Y. J. Yan, "Correlated driving and dissipation in two-dimensional spectroscopy," J. Chem. Phys. **138**, 024106 (2013).
- ¹⁷ Y. J. Yan, "Theory of open quantum systems with bath of electrons and phonons and spins: Many-dissipaton density matrixes approach," J. Chem. Phys. **140**, 054105 (2014).
- ¹⁸ H. D. Zhang, R. X. Xu, X. Zheng, and Y. J. Yan, "Nonperturbative spin-boson and spin-spin dynamics and nonlinear Fano interferences: A unified dissipaton theory based

- study," J. Chem. Phys. 142, 024112 (2015).
- ¹⁹ Y. Tanimura and R. Kubo, "Time evolution of a quantum system in contact with a nearly Gaussian-Markovian noise bath," J. Phys. Soc. Jpn. 58, 101 (1989).
- ²⁰ Y. Tanimura, "Nonperturbative expansion method for a quantum system coupled to a harmonic-oscillator bath," Phys. Rev. A **41**, 6676 (1990).
- ²¹ A. Ishizaki and Y. Tanimura, "Quantum dynamics of system strongly coupled to low temperature colored noise bath: Reduced hierarchy equations approach," J. Phys. Soc. Jpn. **74**, 3131 (2005).
- ²² Y. Tanimura, "Stochastic Liouville, Langevin, Fokker-Planck, and master equation approaches to quantum dissipative systems," J. Phys. Soc. Jpn. **75**, 082001 (2006).
- ²³ Y. A. Yan, F. Yang, Y. Liu, and J. S. Shao, "Hierarchical approach based on stochastic decoupling to dissipative systems," Chem. Phys. Lett. **395**, 216 (2004).
- ²⁴ R. X. Xu, P. Cui, X. Q. Li, Y. Mo, and Y. J. Yan, "Exact quantum master equation via the calculus on path integrals," J. Chem. Phys. **122**, 041103 (2005).
- ²⁵ R. X. Xu and Y. J. Yan, "Dynamics of quantum dissipation systems interacting with bosonic canonical bath: Hierarchical equations of motion approach," Phys. Rev. E 75, 031107 (2007).
- ²⁶ J. J. Ding, R. X. Xu, and Y. J. Yan, "Optimizing hierarchical equations of motion for quantum dissipation and quantifying quantum bath effects on quantum transfer mechanisms," J. Chem. Phys. **136**, 224103 (2012).
- ²⁷ Y. Tanimura, "Numerically "exact" approach to open quantum dynamics: The hierarchical equations of motion (HEOM)," J. Chem. Phys 153, 020901 (2020).
- ²⁸ Y. J. Yan, J. S. Jin, R. X. Xu, and X. Zheng, "Dissipaton equation of motion approach to open quantum systems," Frontiers Phys. **11**, 110306 (2016).
- ²⁹ Y. Wang, R. X. Xu, and Y. J. Yan, "Entangled systemand-environment dynamics: Phase-space dissipaton theory," J. Chem. Phys. **152**, 041102 (2020).
- ³⁰ Z.-H. Chen, Y. Wang, R.-X. Xu, and Y. Yan, "Correlated vibration-solvent effects on the non-Condon exciton spectroscopy," J. Chem. Phys. **154**, 244105 (2021).
- ³¹ Y. Wang, Z. J. Pan, H. D. Zhang, and Y. J. Yan, "Dissipaton dynamics theory versus quantum master equations," Chem. Phys. **515**, 94 (2018).
- ³² S. H. Lin and H. Eyring, "Study of the Franck-Condon and Herzberg-Teller approximations," Proc. Nat. Acad. Sci. USA **71**, 3802 (1974).
- ³³ H. D. Zhang, Q. Qiao, R. X. Xu, and Y. J. Yan, "Effects of Herzberg–Teller vibronic coupling on coherent excitation energy transfer," J. Chem. Phys. **145**, 204109 (2016).
- ³⁴ S. Mukamel, The Principles of Nonlinear Optical Spectroscopy, Oxford University Press, New York, 1995.
- ³⁵ L. P. Chen, R. H. Zheng, Q. Shi, and Y. J. Yan, "Optical line shapes of molecular aggregates: Hierarchical equations of motion method," J. Chem. Phys. **131**, 094502 (2009).