

Constructing quantum dynamics from mixed quantum-classical descriptions

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Abstract

The influence of quantum bath effects on the dynamics of a quantum two-level system linearly coupled to a harmonic bath is studied when the coupling is both diagonal and off-diagonal. It is shown that the pure dephasing kernel and the non-adiabatic quantum transition rate between Born–Oppenheimer states of the subsystem can be decomposed into a contribution from thermally excited bath modes plus a zero point energy contribution. This quantum rate can be modewise factorized exactly into a product of a mixed quantum subsystem-classical bath transition rate and a quantum correction factor. This factor determines dynamics of quantum bath correlations. Quantum bath corrections to both the transition rate and the pure dephasing kernel are shown to be readily evaluated via a mixed quantum-classical simulation. Hence, quantum dynamics can be recovered from a mixed quantum-classical counterpart by incorporating the missing quantum bath corrections. Within a mixed quantum-classical framework, a simple approach for evaluating quantum bath corrections in calculation of the non-adiabatic transition rate is presented.

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1. Introduction

In this work, we study the influence of quantum bath effects on the dynamics of the quantum subsystem using a popular model of a two-level system linearly coupled to the harmonic bath. We address an important issue of quantum-classical correspondence in the context of non-adiabatic (NA) transitions in condensed phase environments with the emphasis on the role of quantum corrections in calculation of NA transition rates and evaluation of pure dephasing within a mixed quantum-classical treatment.

A primary quantum bath effect directly related to the NA transition rates and pure dephasing is quantum decoherence (loss of quantum correlation) in the degrees of freedom of the environment, when coupled to the two-level system. Interaction of the system with the environment brings about the appearance of certain classical

features at the expense of quantum correlations [1,2]. The problem of quantum coherence gave a significant stimulus to numerous studies of simple quantum systems [3–5]. In relation to NA molecular dynamics (MD) simulations, neglecting the quantum corrections can result in both quantitative and qualitative errors [4–6].

Another manifestation of the quantum nature of a harmonic bath is zero point energy [6,7]. At low temperature, the lowest excited states of the bath modes are mostly populated, and the effect of zero point motion is pronounced. The role of zero point motion can be significant even at room temperatures, if high frequency modes of the bath are coupled to the quantum system. The neglect of a contribution from zero point energy may lead to an underestimation of the quantum NA transition rates and pure dephasing. In the context of NA MD simulations, zero point motion can be another source of disagreement between the exact quantum and mixed quantum-classical treatment.

We study the NA transitions employing a model of a two-level system coupled to a harmonic bath [8–12]. This model has been extensively treated in literature [13–18]. In the present work, we consider a general case

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when the system-bath coupling is both diagonal and off-diagonal in the basis of two-level eigenstates. The diagonal coupling includes displacements of the equilibrium positions of the bath modes associated with initial and final states potential surfaces. The off-diagonal interaction is realized via the NA coupling of the two-level system to momenta of the bath modes. Most recently, this model was used by Egorov et al. [19] to probe the accuracy of several mixed quantum-classical approximations in calculating the NA transition rates, and by Golosov and Reichman [20] in their master equation approach to charge transfer processes. We study the impact of quantum bath effects on the dynamics of the quantum system by following the evolution of the two-level system in the relaxation time scale. We utilize the Liouville–von Neumann formulation of quantum mechanics. This formalism allows to study an approach to equilibrium in both classical and quantum systems [21–25] and thus, facilitates the study of quantum-classical correspondence.

A common approach to studies of quantum dynamics in the condensed phases is to utilize a mixed quantum-classical treatment (i.e., quantum subsystem in a classical bath). These methods provide a theoretical background for various quantum-classical MD schemes widely implemented in studies of inter- and intramolecular transfer and redistribution of energy in condensed media chemical systems [4–6,26–30]. Within this treatment, one estimates the full quantum (FQ) rates from the results of mixed quantum-classical simulations. In general, the exact solution to this problem is not known. To take into account quantum bath effects, several approximate schemes have been proposed [6,27,28], and due to the approximate nature of these mixed quantum-classical schemes, it is important to establish their accuracy.

Prezhdo and Rossky [6] have used Kubo’s generating function method [31] to examine the source of limitations of mixed quantum-classical approaches in studies of NA transitions. Prezhdo and Rossky [6] approximated wave functions of the bath modes by frozen Gaussians. In the present work, we put this result on an analytical foundation. Using the model of a two-level quantum system coupled to a harmonic bath, we analytically establish the validity of mixed quantum-classical approximations in evaluating the quantum NA transition rate. We extend the validity of a mixed quantum-classical treatment to evaluating pure dephasing. We show that the quantum NA transition rate for the present model admits factorization into its mixed quantum-classical counterpart and a “quantum bath correction factor”, a well-defined quantity encapsulating all the quantum features of the bath. We show that quantum bath corrections to both the NA transition rate and pure dephasing can be expressed in terms of classical quantities and thus, are readily evaluated within a mixed quantum-classical framework. Hence, one is able to “repair” a mixed

quantum-classical treatment to reproduce the true quantum dynamics.

The model is described in Section 2. In Section 3, we derive the master equation for the reduced density matrix and analyze the FQ NA transition rate and the pure dephasing kernel. In Section 4, we present an approach to evaluating quantum bath corrections in terms of classical quantities in calculation of the NA transition rate and pure dephasing. A numerical example is presented in Section 5. In Section 6 we conclude. Technical details are given in Appendices.

2. The model

Consider a two-level system given by the ground $|0\rangle$ and excited $|1\rangle$ states with the energy splitting $\hbar\omega_{el}$, coupled to a set of harmonic oscillators with masses m_j and frequencies ω_j , $j = 1, 2, \dots, N$. The Hamiltonian is

$$H = H_0 + V, \quad (1)$$

where

$$H_0 = H_e|1\rangle\langle 1| + H_g|0\rangle\langle 0| \\ = (H_b + \hbar\omega_{el})|1\rangle\langle 1| + (H_b + \Delta)|0\rangle\langle 0| \quad (2)$$

and

$$V = V_{01}|0\rangle\langle 1| + V_{10}|1\rangle\langle 0|. \quad (3)$$

The H_0 -part of the Hamiltonian stands for the unperturbed energy of the two-level system and the bath, whereas the V -part stands for the “off-diagonal” interaction. We assumed that bath modes are not distorted between states, and ignored mode mixing. Then, the “diagonal” coupling Δ is

$$\Delta = \sum_j m_j \omega_j^2 \delta_j q_j + \frac{1}{2} \sum_j m_j \omega_j^2 \delta_j^2, \quad (4)$$

where q_j and δ_j stand for the coordinate and the displacement of the j th oscillator from its equilibrium position. This form of diagonal coupling would arise when the two potential energy surfaces corresponding to the two states of the two-level system are described by two multidimensional harmonic surfaces which differ only in equilibrium positions. H_b is the bath Hamiltonian,

$$H_b = \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right). \quad (5)$$

We introduce the creation a_j^\dagger and annihilation a_j operators for each j th oscillator of the bath,

$$a_j^\dagger = \left(\frac{m_j \omega_j}{2\hbar} \right)^{1/2} \left(q_j - i \frac{p_j}{m_j \omega_j} \right), \\ a_j = \left(\frac{m_j \omega_j}{2\hbar} \right)^{1/2} \left(q_j + i \frac{p_j}{m_j \omega_j} \right). \quad (6)$$

In Eq. (3) V_{01} and V_{10} represent the weak coupling between adiabatic Born–Oppenheimer states

$$V_{10} = \sum_j -\frac{i\hbar}{m_j} \langle 1|\nabla_j|0\rangle \hat{p}_j = \hbar \sum_j V_j^{10} (a_j^+ - a_j) \quad (7)$$

and $V_{01} = (V_{10})^*$, where $V_j^{10} = \langle 1|\nabla_j|0\rangle (\hbar\omega_j/2m_j)^{1/2}$. Here, $\langle 1|\nabla_j|0\rangle$ is the matrix element of the j th bath mode non-adiabatic coupling with ∇_j being the gradient operator of the j th-bath mode coordinate with respect to the quantum subsystem wave functions. In Eq. (7) we have neglected the j th-bath mode displacement of the equilibrium position δ_j .

The statistical description in quantum mechanics is given by the Liouville–von Neumann equation for the density matrices [22,23]

$$i\frac{\partial}{\partial t}\rho(t) = L_H\rho(t). \quad (8)$$

Here the “Liouvillian” L_H is the commutator with the Hamiltonian, i.e., $L_H\rho = H\rho - \rho H$. We can decompose L_H into an unperturbed part L_0 and an interaction L_V :

$$L_H = L_0 + L_V, \quad (9)$$

where $L_0 = (1/\hbar)(H_0 \times 1 - 1 \times H_0)$ and $L_V = (1/\hbar)(V \times 1 - 1 \times V)$, respectively. For the case where the wave function space is spanned by a complete orthonormal basis $\sum_\alpha |\alpha\rangle\langle\alpha| = 1$, $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$, the Liouville space is spanned by a complete orthonormal basis of the dyads $|\alpha;\beta\rangle \equiv |\alpha\rangle\langle\beta|$, i.e., $\sum_{\alpha,\beta} |\alpha;\beta\rangle\langle\alpha;\beta| = 1$, $\langle\langle\alpha;\beta|\alpha';\beta'\rangle\rangle = \delta_{\alpha\alpha'}\delta_{\beta'\beta}$. The matrix element of an operator A in the wave function space is given by $\langle\langle\alpha;\beta|A\rangle\rangle = \langle\alpha|A|\beta\rangle$. Then, the matrix element of the Liouville operator in the Liouville space is given by

$$\langle\langle\alpha;\beta|L_H|\alpha';\beta'\rangle\rangle = H_{\alpha\alpha'}\delta_{\beta'\beta} - \delta_{\alpha\alpha'}H_{\beta'\beta}, \quad (10)$$

where $H_{\alpha\alpha'} \equiv \langle\alpha|H|\alpha'\rangle = \langle\langle\alpha;\alpha'|H\rangle\rangle$. The basis for the Liouville space in the occupation number representation is given by $|\alpha;\beta\rangle = |l_1, \{n_j\}^N; l'_1, \{n'_j\}^N\rangle$, where l_1, l'_1 and n_j, n'_j are occupation numbers for the excited and ground state Hamiltonians of the quantum system and the bath, respectively.

3. Dephasing and NA transition rates

To derive the master equation for the reduced two-level system density matrix, we introduce the projection operators that specify system-bath correlation components, such as distribution of the l -level system $P_{l_1}^{(v_1)}$, correlations between the l -level system and a single j th-bath mode $P_{l_1, n_j}^{(v_1, v_j)}$, and so on,

$$P_{l_1}^{(v_1)} \equiv \sum_{\{n_j\}} |l_1, \{n_j\}; l'_1, \{n_j\}\rangle\langle\langle l_1, \{n_j\}; l'_1, \{n_j\}|, \quad (11)$$

$$P_{l_1, n_j}^{(v_1, v_j)} \equiv \sum_{\{n_j\}_{(j')}} |l_1, n_j, \{n_j\}_{(j')}; l'_1, n'_j, \{n_j\}_{(j')}\rangle\langle\langle l_1, n_j, \{n_j\}_{(j')}; l'_1, n'_j, \{n_j\}_{(j')}|(1 - \delta_{v_j, 0}), \quad (12)$$

where $v_1 = l'_1 - l_1$, $v_j = n'_j - n_j$. Here $\{n_j\}_{(j', \dots)}$ means that the components n_j, \dots are excluded from the set $\{n_j\} = \{n_1, n_2, \dots\}$. Next, we introduce operators

$$P^{(v_1)} \equiv \sum_{l_1} P_{l_1}^{(v_1)}, \quad P^{(v_1, v_j)} \equiv \sum_{l_1} \sum_{n_j} P_{l_1, n_j}^{(v_1, v_j)}, \dots \quad (13)$$

These are eigenprojectors of L_0 ,

$$L_0 P^{(v_1, v_j, \dots)} = P^{(v_1, v_j, \dots)} L_0 = (v_1\omega_1 + v_j\omega_j + \dots) P^{(v_1, v_j, \dots)} \quad (14)$$

and satisfy the completeness and orthonormality conditions

$$\sum_{v_1} P^{(v_1)} + \sum_{j'} \sum_{v_1, v_j} P^{(v_1, v_j)} + \dots = 1, \quad P^{(v_1, v_j, \dots)} P^{(\mu_1, \mu_j, \dots)} = P^{(v_1, v_j, \dots)} \delta_{v_1, \mu_1} \delta_{v_j, \mu_j} \dots \quad (15)$$

To avoid heavy notation, we introduce the superscript $v \equiv (v_1, v_j, \dots)$, and express (14) as $L_0 P^{(v)} = P^{(v)} L_0 = w^{(v)} P^{(v)}$, where $w^{(v)} \equiv v_1\omega_1 + v_j\omega_j + \dots$. In this notation, the completeness and orthogonality relation (15) become $\sum_v P^{(v)} = 1$ and $P^{(v)} P^{(\mu)} = \delta_{\mu, v} P^{(v)}$.

We also define the complements

$$Q^{(v)} \equiv 1 - P^{(v)} \quad (16)$$

such that $(P^{(v)})^2 = P^{(v)}$, $(Q^{(v)})^2 = Q^{(v)}$, $P^{(v)} Q^{(v)} = Q^{(v)} P^{(v)} = 0$ and $L_0 P^{(v)} = P^{(v)} L_0$, $L_0 Q^{(v)} = Q^{(v)} L_0$. It is useful to decompose the time evolution of the total density matrix as [22,23]

$$P^{(v_1)} \rho(t) = P^{(v_1)} \rho^{(v_1)}(t) + P^{(v_1)} \rho_{np}^{(v_1)}(t). \quad (17)$$

In Eq. (17) the first term on the right-hand side (RHS) is the “privileged” component of the v_1 -correlation subspace [22,23] and obeys the Markovian evolution. The second term is the “non-privileged” component and corresponds to the memory effects which will not be analyzed in the present work. We restrict ourselves to the component of the v_1 -correlation subspace, since it has a dominant contribution to the time evolution in the relaxation time scale [22–25] (second order perturbation theory). Then, the Liouville equation for the total density matrix is

$$i\frac{\partial}{\partial t} P^{(v_1)} \rho^{(v_1)}(t) = \theta^{(v_1)}(z) P^{(v_1)} \rho^{(v_1)}(t), \quad (18)$$

where $\theta^{(v_1)}(z)$ is the collision operator [22,23],

$$\theta^{(v_1)}(z) = P^{(v_1)} L_0 P^{(v_1)} + P^{(v_1)} L_V Q^{(v_1)} \times \frac{1}{w^{(v_1)} - L_0 - i\epsilon} Q^{(v_1)} L_V P^{(v_1)}, \quad (19)$$

where $w_{(v_1)}$ is the eigenvalue of L_0 acting on the eigenprojector $P^{(v_1)}$. Hereafter, we abbreviate $\rho^{(v_1)}$ as ρ . We assume that at the time $t = 0$ the total density matrix is a direct product

$$\rho(l_1, \{n_j\}^N; l'_1, \{n'_j\}^N; 0) = \rho_s(l_1, l'_1, 0) \otimes \prod_j \rho_b(n_j, n'_j, 0) \quad (20)$$

where $\rho_s(l_1, l'_1, 0)$ and $\rho_b(n_j, n'_j, 0)$ are the reduced quantum subsystem and the j th-mode of the bath density matrices at time $t = 0$, respectively.

Equations of motion for the coherence $\rho_s(1, 0, t)$ and the excited state population $\rho_s(1, 1, t)$ enable us to estimate the dephasing and the NA transition time scales, respectively. These equations are derived in Appendix A using Liouville space diagrams. We obtain:

$$\rho_s(1, 0, t) = \rho_s(1, 0)_0 e^{-i\tilde{\omega}_{el}t} C(t) e^{-\frac{1}{2}k_{1\rightarrow 0}^{\text{qm}}t}, \quad (21)$$

where $\rho_s(1, 0)_0$ is $\rho_s(1, 0)$ at the time $t = 0$. The renormalized frequency is

$$\tilde{\omega}_{el} = \omega_{el} + \delta\omega_{el} \quad (22)$$

with the ‘‘off-diagonal’’ frequency shift ($|\delta\omega_{el}| \ll \omega_{el}$) due to the NA system-bath coupling given by

$$\delta\omega_{el} = - \sum_j \sum_{\{m_j\}} |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \times P \left(\frac{1}{\Delta E - \hbar\omega_{el}} \right), \quad (23)$$

where P denotes the principal part and ΔE is the bath energy gap. In Eq. (21) we have defined the quantum correlation function

$$C(t) \equiv \text{Tr}_b \left[\rho_b \exp_T \left\{ \frac{i}{\hbar} \int_0^t \Delta(t) dt \right\} \right], \quad (24)$$

where $\Delta(t) = \exp[iH_b t/\hbar] \Delta \exp[-iH_b t/\hbar]$; T stands for time ordering and $\text{Tr}_b[\rho_b \dots]$ denotes thermal average. $C(t)$ plays an important role in the forthcoming analysis of NA transition rates, and is discussed in the next section. The explicit evaluation of $C(t)$ has been done by many authors [14,15,17–19,27,31,32]. Up to the second order in the cumulant expansion we have $(\beta = (k_B T)^{-1})$ [32]

$$\begin{aligned} C(t) &= \exp \left\{ \sum_j \frac{m_j \omega_j \delta_j^2}{2\hbar} [(2\bar{n}_j + 1)(\cos \omega_j t - 1) \right. \\ &\quad \left. - i \sin \omega_j t] \right\} \\ &= \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega \left[\coth \frac{\beta \hbar \omega}{2} (\cos \omega t - 1) \right. \right. \\ &\quad \left. \left. - i \sin \omega t \right] \right\}, \quad (25) \end{aligned}$$

where \bar{n}_j is the mean occupation number of the j th-bath mode at temperature T , i.e., $\bar{n}_j = [\exp(\hbar\omega_j/k_B T) - 1]^{-1}$,

and we have defined the ‘‘diagonal’’ spectral density $J(\omega)$,

$$J(\omega) = \sum_j \delta(\omega - \omega_j) m_j \delta_j^2. \quad (26)$$

Since the diagonal coupling is linear in bath coordinates, Eq. (25) is exact to any order in the cumulant expansion [32]. In Eq. (21) the quantum NA transition rate is

$$\begin{aligned} k_{1\rightarrow 0}^{\text{qm}} &= \frac{2\pi}{\hbar} \text{Tr}_b \left[\rho_b \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \right. \\ &\quad \left. \times \delta(\Delta E - \hbar\omega_{el}) [(n_j + 1)_t + (n_j)_t] \right]. \quad (27) \end{aligned}$$

Franck–Condon factors $|\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2$ appearing in Eq. (27) contain all the information about quantum coherence in variables of the bath, and are evaluated in the next section.

Eq. (27) for $k_{1\rightarrow 0}^{\text{qm}}$ appears naturally as a sum $k_{1\rightarrow 0}^{\text{qm}} = k_{01} + k_{10}$ of ‘‘down’’ ($k_{01} \sim (n_j + 1)_t$) and ‘‘up’’ ($k_{10} \sim (n_j)_t$) NA transition rates where $(n_j + 1)_t = (n_j + 1) \exp[-i\omega_j t]$ and $(n_j)_t = n_j \exp[i\omega_j t]$. Here, the down rate $k_{01} \neq 0$ as $T \rightarrow 0$ (spontaneous emission). Using the fact that $\bar{n}_j + 1 = \bar{n}_j \exp[\beta \hbar \omega_j]$, we see that upon performing thermal averaging in Eq. (27), we recover detailed balance satisfied for each j th-bath mode. Note that in Eq. (27) for $k_{1\rightarrow 0}^{\text{qm}}$, we may also separate contributions from the thermally excited bath modes and zero point energy (see also [7]) into a quantum high energy (qhe) NA transition rate $k_{1\rightarrow 0}^{\text{qhe}}$ and a zero point energy (zpe) correction $k_{1\rightarrow 0}^{\text{zpe}}$, i.e., $k_{1\rightarrow 0}^{\text{qm}} = k_{1\rightarrow 0}^{\text{qhe}} + k_{1\rightarrow 0}^{\text{zpe}}$, where

$$\begin{aligned} k_{1\rightarrow 0}^{\text{qhe}} &= \frac{2\pi}{\hbar} \text{Tr}_b \left[\rho_b \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \right. \\ &\quad \left. \times \delta(\Delta E - \hbar\omega_{el}) 2n_{j0} \cos \omega_j t \right] \quad (28) \end{aligned}$$

and

$$\begin{aligned} k_{1\rightarrow 0}^{\text{zpe}} &= \frac{2\pi}{\hbar} \text{Tr}_b \left[\rho_b \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \right. \\ &\quad \left. \times \delta(\Delta E - \hbar\omega_{el}) (\cos \omega_j t - i \sin \omega_j t) \right], \quad (29) \end{aligned}$$

n_{j0} is the occupation number of the j th-mode at $t = 0$. The zero point energy contribution (29) is important at low temperature where primarily the lower excited states of bath modes are populated, or even at room temperature if the two-level system interacts with high

frequency modes. Let us study the evolution of the excited state. The equation of motion for $\rho_s(1, 1, t)$ is

$$\rho_s(1, 1, t) = \frac{1}{2} \frac{k_{1 \rightarrow 0}^{\text{qhc}}}{k_{1 \rightarrow 0}^{\text{qm}}} (1 - e^{-k_{1 \rightarrow 0}^{\text{qm}} t}) + \rho_s(1, 1)_0 e^{-k_{1 \rightarrow 0}^{\text{qm}} t}, \quad (30)$$

where $\rho_s(1, 1)_0$ is $\rho_s(1, 1)$ at $t = 0$. In the limit of large t , we obtain

$$\rho_s(1, 1, t) \rightarrow \frac{1}{2} \frac{k_{1 \rightarrow 0}^{\text{qhc}}}{k_{1 \rightarrow 0}^{\text{qhc}} + k_{1 \rightarrow 0}^{\text{zpc}}}. \quad (31)$$

At high temperature $n_j \gg 1$, $\rho_s(1, 1, t) \rightarrow 1/2$, and the two-level system wave function becomes a superposition of the excited and ground states. In contrast, at low temperature $n_j \ll 1$, $\rho_s(1, 1, t) \rightarrow 0$, and the same wave function is dominated by the ground state contribution. We would have obtained the incorrect time dependence for $\rho_s(1, 1, t)$, had we neglected the zero point energy contribution. We would have obtained $\rho_s(1, 1, t) \rightarrow 1/2$ in both limits. This implies that the neglect of zero point motion is inconsistent with the dynamics (no spontaneous emission at zero temperature) and violates the detailed balance condition [16].

Let us now study the coherence. In the exponent in Eq. (25) for the quantum correlation function, the imaginary part can be viewed as the “diagonal” frequency shift. This part of the two-level system frequency modulation is due to the adiabatic fluctuations in the total energy gap

$$\delta\omega'_{\text{el}}(t) = -\frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega \sin \omega t. \quad (32)$$

The real part in the exponent in Eq. (25) corresponds to pure dephasing [14,15,17,18]

$$\begin{aligned} d(t) &= -\sum_j \frac{m_j \omega_j \delta_j^2}{2\hbar} (2\bar{n}_j + 1) (1 - \cos \omega_j t) \\ &= -\frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega \coth \frac{\beta\hbar\omega}{2} (1 - \cos \omega t). \end{aligned} \quad (33)$$

As in the case of the FQ NA transition rate in Eq. (33), we may separate contributions from the thermally excited bath modes and zero point energy. Indeed, in the limit of zero temperature ($\coth \beta\hbar\omega/2 \rightarrow 1$) we obtain the zero point energy contribution to pure dephasing, $d^{\text{zpc}}(t) = 1/2\hbar \int_0^\infty d\omega J(\omega) \omega (\cos \omega t - 1)$, a result previously obtained by Reichman et al. [17].

For strong diagonal coupling, we can expand $\sin \omega t$ and $\cos \omega t$ in Taylor series retaining terms to second order in time, and Eq. (21) for $\rho_s(1, 0, t)$ becomes

$$\rho_s(1, 0, t) \approx \rho_s(1, 0)_0 e^{-i\tilde{\omega}_{\text{el}} t} e^{-dt^2} e^{-\frac{1}{2}k_{1 \rightarrow 0}^{\text{qm}} t} \quad (34)$$

with

$$\tilde{\omega}_{\text{el}} = \omega_{\text{el}} + \delta\omega_{\text{el}} + \delta\omega'_{\text{el}} = \tilde{\omega}_{\text{el}} + \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega^2 \quad (35)$$

and

$$d = \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \frac{\omega^3}{2} \coth \frac{\beta\hbar\omega}{2}. \quad (36)$$

If the two-level system wave function is given by a linear superposition of eigenstates, $|\Psi_s\rangle = c_0|0\rangle + c_1|1\rangle$, then the off-diagonal elements of the reduced density matrix undergo a trivial “rotation” due to the factor $\exp[-i\tilde{\omega}_{\text{el}}t]$, and decay in time as a result of decrease of the “correlation amplitude” $\exp[-1/2k_{1 \rightarrow 0}^{\text{qm}}t - dt^2]$ (total dephasing). Here, we have three time scales. For times of the order of the inverse of the two-level system renormalized frequency, $t \sim 1/\tilde{\omega}_{\text{el}}$, $\rho_s(1, 0, t)$ undergoes unitary evolution. For times longer than the inverse of the renormalized frequency and of the order of the pure dephasing time ($\tau_{\text{deph}} = d^{-1/2}$), $1/\tilde{\omega}_{\text{el}} \ll t \sim \tau_{\text{deph}}$, the dynamics of phase coherence is determined by pure dephasing with a quadratic time dependence ($\sim \exp[-(t/\tau_{\text{deph}})^2]$). Finally, for times of the order of the inverse of the quantum NA transition rate $t \sim 1/k_{1 \rightarrow 0}^{\text{qm}}$, the phase coherence undergoes an exponential decay ($\sim \exp[-1/2k_{1 \rightarrow 0}^{\text{qm}}t]$). As time progresses, the correlation amplitude decays to zero, and a superposition of eigenstates *dynamically* evolves into a statistical mixture: $|\Psi_s\rangle\langle\Psi_s| \rightarrow |c_0|^2|0\rangle\langle 0| + |c_1|^2|1\rangle\langle 1|$.

4. FQ vs mixed quantum-classical treatment

Within the framework of MD calculation of the NA transition rates, one is faced with the problem of inferring the FQ rate from results of the mixed quantum-classical simulations. In the context of calculating the NA transition rates, evaluation of quantum corrections renders “factorizability” of the FQ rate into its mixed quantum-classical counterpart times a factor which encompasses all quantum features of the thermal bath. To show this in Eq. (27) we evaluate the Franck–Condon factors and sum over the final states. We obtain

$$\begin{aligned} k_{1 \rightarrow 0}^{\text{qm}} &= \text{Tr} \left[\rho_b \sum_j |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t} [(n_j + 1)_t + (n_j)_t] \right. \\ &\quad \left. \times \prod_j \langle n_j | e^{iH_b t/\hbar} e^{-i(H_b + \Delta)t/\hbar} | n'_j \rangle \right] \\ &= \sum_j \left\langle |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t} [(n_j + 1)_t + (n_j)_t] \right. \\ &\quad \left. \times \exp_T \left\{ -\frac{i}{\hbar} \int_0^t dt' \Delta(t') \right\} \right\rangle. \end{aligned} \quad (37)$$

We had already encountered the last factor appearing in the second line on the RHS in Eqs. (21) and (25). This is the quantum correlation function given by the time-ordered exponential of the difference in action associated with the initial and final state potential surfaces,

$C(t) = \langle \prod_j \langle n_j(t) | n'_j(t) \rangle \rangle_T = \langle \exp_T \{ -i/\hbar \int dt \Delta(t) \} \rangle_T$. Microscopically, this function is the thermally averaged product of the bath mode initial and final state wave functions and therefore determines the dynamics of quantum bath correlations. As these wave functions cease to overlap, these correlations vanish [6].

To compute a mixed quantum-classical counterpart to the FQ NA transition rate, we take the “classical bath limit” (i.e., the classical limit $\hbar \rightarrow 0$ in variables of the bath) in the quantum correlation function $C(t)$ in Eq. (37). Calculation is presented in Appendix B. We obtain

$$\begin{aligned} k_{1 \rightarrow 0}^{\text{q-c}} &= \text{Tr}_b \left[\rho_b \sum_j |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t} [(n_j + 1)_t + (n_j)_t] \right. \\ &\quad \times \left. \left\{ \lim_{\hbar \rightarrow 0} \prod_j \langle n_j(t) | n'_j(t) \rangle \right\} \right] \\ &= \sum_j \left\langle |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t} [(n_j + 1)_t + (n_j)_t] \right. \\ &\quad \times \left. \exp \left\{ -\frac{i}{\hbar} \int_0^{t'} dt \Delta(t) \right\} \right\rangle_T. \end{aligned} \quad (38)$$

Note that in the above expression, the time-ordered exponential appearing in the RHS of Eq. (37) is replaced with the usual classical correlation function. A similar expression for $k_{1 \rightarrow 0}^{\text{q-c}}$ with a (higher order) contribution from displacement of the bath mode equilibrium positions to the amplitude of the off-diagonal coupling has been discussed by Egorov et al. [19,33], and without zero point energy contribution by Staib and Borgis [28]. For the case of static off-diagonal coupling, the expression for $k_{1 \rightarrow 0}^{\text{q-c}}$ (without a prefactor $[(n_j + 1)_t + (n_j)_t]$) has been exploited by many authors [19,27,32–34].

We now proceed to derive an analytic expression relating the FQ and mixed quantum-classical NA transition rates. We start from expressions (37) and (38) for $k_{1 \rightarrow 0}^{\text{qm}}$ and $k_{1 \rightarrow 0}^{\text{q-c}}$, and introduce the FQ ($\xi_{1 \rightarrow 0, j}^{\text{qm}}$) and mixed quantum-classical ($\xi_{1 \rightarrow 0, j}^{\text{q-c}}$) rates defined for each j th-bath mode

$$\xi_{1 \rightarrow 0, j}^{\text{qm}} = |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t - \frac{i}{\hbar} \int_0^{t'} \Delta(t) dt} [(n_j + 1)_t + (n_j)_t] Q(t) \quad (39)$$

and

$$\xi_{1 \rightarrow 0, j}^{\text{q-c}} = |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t - \frac{i}{\hbar} \int_0^{t'} \Delta(t) dt} [(n_j + 1)_t + (n_j)_t], \quad (40)$$

such that $k_{1 \rightarrow 0}^{\text{qm}} = \sum_j \langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \rangle_T$ and $k_{1 \rightarrow 0}^{\text{q-c}} = \sum_j \langle \xi_{1 \rightarrow 0, j}^{\text{q-c}} \rangle_T$. In Eqs. (39) and (40) we have defined the “quantum bath correction factor” $Q(t)$,

$$Q(t) \equiv \frac{\exp_T \left\{ -\frac{i}{\hbar} \int_0^{t'} dt \Delta(t) \right\}}{\exp \left\{ -\frac{i}{\hbar} \int_0^{t'} dt \Delta(t) \right\}}. \quad (41)$$

Comparing now expressions (39) and (40) for $\xi_{1 \rightarrow 0, j}^{\text{qm}}$ and $\xi_{1 \rightarrow 0, j}^{\text{q-c}}$, we obtain the following “factorization”:

$$k_{1 \rightarrow 0}^{\text{qm}} = \sum_j \left\langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \right\rangle_T = \sum_j \langle \xi_{1 \rightarrow 0, j}^{\text{q-c}} [Q(t)] \rangle_T. \quad (42)$$

The above expression is one of the main results of the present work. Considering the form of Eq. (42), factorization should be understood as a modewise Fourier transformation of the NA coupling amplitude weighted quantum bath correction factor. The weight $[(n_j + 1)_t + (n_j)_t]$ determines a share of the j th-bath mode contribution to the NA transition amplitude in the total FQ rate. The quantum correction factor $Q(t)$ takes into account *all* quantum features of the thermal bath ignored in a mixed quantum-classical evaluation of the NA transition rate, and is given as a ratio of the FQ correlation function to its quantum-classical counterpart.

Factorization (42) provides analytical grounds for evaluating the quantum bath corrections. Note also that it is exact, i.e., summing over all thermally averaged rates for each j th-bath mode

$$\begin{aligned} \langle \xi_{1 \rightarrow 0, j}^{\text{q-c}} [Q(t)] \rangle_T &= \langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \rangle_T \\ &= |V_j^{10}|^2 \int dt e^{i\omega_{\text{el}} t} \left[\coth \frac{\beta \hbar \omega_j}{2} \cos \omega_j t - i \sin \omega_j t \right] \\ &\quad \times \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega \left[\coth \frac{\beta \hbar \omega}{2} \right. \right. \\ &\quad \times \left. \left. (\cos \omega t - 1) - i \sin \omega t \right] \right\} \end{aligned} \quad (43)$$

we recover the FQ rate

$$\begin{aligned} k_{1 \rightarrow 0}^{\text{qm}} &= \sum_j \langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \rangle_T \\ &= \int d\omega J'(\omega) \int dt e^{i\omega_{\text{el}} t} \left[\coth \frac{\beta \hbar \omega}{2} \cos \omega t - i \sin \omega t \right] \\ &\quad \times \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega) \omega \left[\coth \frac{\beta \hbar \omega}{2} (\cos \omega t - 1) \right. \right. \\ &\quad \times \left. \left. - i \sin \omega t \right] \right\}, \end{aligned} \quad (44)$$

where following Egorov et al. [19], in addition to the spectral density $J(\omega)$, we have defined the other (off-diagonal) spectral density $J'(\omega)$,

$$J'(\omega) = \sum_j |V_j^{10}|^2 \delta(\omega - \omega_j). \quad (45)$$

We now proceed to presenting a simple perturbative approach that accounts for quantum harmonic bath corrections. This approach can be implemented in calculation of NA transition rates within a mixed

quantum-classical framework. Consider the high temperature approximation to the quantum correlation function $C(t)$. Within this approximation, the thermal weight in $C(t)$ is given by the first order term ($2/\beta\hbar\omega$) in the Taylor expansion of $\coth \beta\hbar\omega/2$. This allows us to rewrite $C(t)$ as

$$\begin{aligned} C(t) &\equiv C^{\text{ht}}(t)Q(t) \\ &= \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{2}{\beta\hbar}\omega(\cos\omega t - 1) - i\sin\omega t \right] \right\} \\ &\quad \times \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\left[\frac{\beta\hbar\omega}{6} + \dots \right] (\cos\omega t - 1) \right] \right\}, \end{aligned} \quad (46)$$

where the first exponential factor appearing on the RHS of the second equality is the high temperature approximation to the quantum correlation function $C^{\text{ht}}(t)$. Note that $C^{\text{ht}}(t)$ differs from $C(t)$ in that the quantum ensemble averaging over initial states of the bath is replaced by the classical ensemble averaging over initial position and momentum. The second exponential factor stands for the low temperature quantum bath correction to $C^{\text{ht}}(t)$, and is given by $Q(t)$. Since $C^{\text{ht}}(t)$ takes care of high temperature contributions, $Q(t)$ picks up low temperature corrections to the decay of quantum bath correlations.

As $\beta\hbar\omega$ is a measure of importance of quantum bath effects ($\hbar\omega$) compared with the characteristic thermal motion (β^{-1}), we Taylor expand $Q(t)$ in Eq. (46) in powers of the exponent. Then, substituting the resulting expression into Eq. (43), we obtain a relation reflecting Bohr's correspondence principle for NA transition rates

$$\begin{aligned} \langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \rangle &= |V_j^{10}|^2 \int dt e^{i\omega_j t} \left[\coth \frac{\beta\hbar\omega_j}{2} \cos \omega_j t - i \sin \omega_j t \right] \\ &\quad \times \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{2}{\beta\hbar\omega} \right. \right. \\ &\quad \times (\cos \omega t - 1) - i \sin \omega t \left. \left. \right] \right\} \\ &\quad \times \left\{ 1 + \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{\beta\hbar\omega}{6} + \dots \right] \right. \\ &\quad \times (\cos \omega t - 1) + \dots \left. \right\}. \end{aligned} \quad (47)$$

In Eq. (47) the first term of the expansion corresponds to the high temperature limit (HT) of $\langle \xi_{1 \rightarrow 0, j}^{\text{qm}} \rangle$, and is given by HT NA transition rate

$$\begin{aligned} \langle \xi_{1 \rightarrow 0, j}^{\text{ht}} \rangle &= |V_j^{10}|^2 \int dt e^{i\omega_j t} \left[\coth \frac{\beta\hbar\omega_j}{2} \cos \omega_j t - i \sin \omega_j t \right] \\ &\quad \times \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{2}{\beta\hbar\omega} (\cos \omega t - 1) \right. \right. \\ &\quad \left. \left. - i \sin \omega t \right] \right\}. \end{aligned} \quad (48)$$

The rest of the terms are quantum corrections to $\langle \xi_{1 \rightarrow 0, j}^{\text{ht}} \rangle$, and to the lowest order are given by

$$\begin{aligned} \langle \xi_{1 \rightarrow 0, j}^{\text{c}} \rangle &= |V_j^{10}|^2 \int dt e^{i\omega_j t} \left[\coth \frac{\beta\hbar\omega_j}{2} \cos \omega_j t - i \sin \omega_j t \right] \\ &\quad \times [\ln Q^{\text{ht}}(t)] \exp \left\{ \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \right. \\ &\quad \times \left. \left[\frac{2}{\beta\hbar\omega} (\cos \omega t - 1) - i \sin \omega t \right] \right\} \end{aligned} \quad (49)$$

with

$$\begin{aligned} \ln Q^{\text{ht}}(t) &= \frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{\beta\hbar\omega}{6} + \dots \right] (\cos \omega t - 1) \\ &= \sum_j \frac{m_j \omega_j \delta_j^2}{2\hbar} \left\{ \frac{\beta\hbar\omega_j}{6} + \dots \right\} (\cos \omega_j t - 1). \end{aligned} \quad (50)$$

Since in Eqs. (49) and (50) the *classical* HT correlation function $C^{\text{ht}}(t)$ is corrected by the factor $\ln Q^{\text{ht}}(t)$ given by the real part of the exponent of $C^{\text{ht}}(t)$ with the statistical weight adjusted as $2/\beta\hbar\omega_j \rightarrow [\beta\hbar\omega_j/6 + \dots]$ for each j th-bath mode, *quantum* corrections are now expressed in terms of the *classical* correlation function and thus, can be computed within the same mixed quantum-classical method.

Let us now turn to analyzing the pure dephasing kernel (see Eq. (33)). Since the real part in the exponent of $C(t)$ determines the pure dephasing kernel (33), the HT approximation can also be used to evaluate pure dephasing within a mixed quantum-classical framework. We obtain

$$\begin{aligned} d(t) &= -\frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{2}{\beta\hbar\omega} + \frac{\beta\hbar\omega}{6} + \dots \right] (1 - \cos \omega t) \\ &= d^{\text{ht}}(t) + d^{\text{c}}(t) \end{aligned} \quad (51)$$

with

$$d^{\text{ht}}(t) = -\frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \frac{2}{\beta\hbar\omega} (1 - \cos \omega t), \quad (52)$$

$$d^{\text{c}}(t) = -\frac{1}{2\hbar} \int_0^\infty d\omega J(\omega)\omega \left[\frac{\beta\hbar\omega}{6} + \dots \right] (1 - \cos \omega t). \quad (53)$$

In Eq. (51), $d^{\text{ht}}(t)$ corresponds to the HT approximation to the pure dephasing and $d^{\text{c}}(t)$ represents the low temperature quantum bath corrections to $d^{\text{ht}}(t)$. As in the case of the NA transition rate, both terms can be readily evaluated within a mixed quantum-classical treatment.

Within the HT method, the time correlation function $C^{\text{ht}}(t)$ can be calculated by using a standard MD propagation scheme by replacing the quantum thermal ensemble averaging over the initial bath states with the classical ensemble average over the position and momentum of bath modes propagated with the arithmetic average of the initial and final state unperturbed

Hamiltonians. Thus, our HT semiclassical approximation is equivalent to the average classical limit (or ACL approximation) previously considered by Egorov et al. [19,35].

The results obtained in this section allow us to conclude, and this is the main result of the present work, that within the harmonic bath approximation, and with a constant non-adiabatic electronic coupling matrix element, the quantum bath corrections to both the NA transition rate and the pure dephasing kernel can be evaluated within a mixed quantum-classical framework. These quantities govern the dynamics of the quantum system phase coherences and population. The separability of the quantum corrections allows for a well defined approximation in which only the quantum component is evaluated in the harmonic approximation, based on accurate classical simulation. This provides a well prescribed formalism in the same spirit as alternative approximate forms implemented earlier [6,7,27,34].

5. Numerical example

To see that the semiclassical approximation derived in the previous section can be accurate in low order, we compare here the FQ NA transition rate for the slightly simpler case of static off-diagonal coupling [19,31]

$$k_{1 \rightarrow 0}^{\text{qm}} \equiv |V^{10}|^2 \int_{-\infty}^{+\infty} dt e^{i\omega_{\text{el}} t} \exp \left[\frac{1}{2\hbar} \int_0^{\infty} d\omega J(\omega) \right] \times \left[\coth \frac{\beta\hbar\omega}{2} (\cos \omega t - 1) - i \sin \omega t \right] \quad (54)$$

with the HT NA transition rate [35]

$$k_{1 \rightarrow 0}^{\text{ht}} \equiv |V^{10}|^2 \int_{-\infty}^{+\infty} dt e^{i\omega_{\text{el}} t} \exp \left[\frac{1}{2\hbar} \int_0^{\infty} d\omega J(\omega) \omega \right] \times \left[\frac{2}{\beta\hbar\omega} (\cos \omega t - 1) - i \sin \omega t \right] \quad (55)$$

adjusted by including the lowest order quantum bath corrections, namely

$$k_{1 \rightarrow 0}^{\text{c}} \equiv |V^{10}|^2 \int_{-\infty}^{+\infty} dt e^{i\omega_{\text{el}} t} \ln[Q_1(t)] \exp \left[\frac{1}{2\hbar} \int_0^{\infty} d\omega J(\omega) \omega \right] \times \left[\frac{2}{\beta\hbar\omega} (\cos \omega t - 1) - i \sin \omega t \right]. \quad (56)$$

The quantum bath correction factor, to lowest order, is

$$Q_1(t) \equiv \exp \left[\frac{1}{2\hbar} \int_0^{\infty} J(\omega) \omega \frac{\beta\hbar\omega}{6} (\cos \omega t - 1) \right], \quad (57)$$

where subscript 1 denotes the first order correction. Following earlier work by Egorov et al. [35], we chose a Gaussian spectral density for harmonic bath modes

$$J(\omega) = \frac{A}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{(\omega - \langle\omega\rangle)^2}{2\sigma^2} \right] \quad (58)$$

with the width σ , centered around the average bath frequency $\langle\omega\rangle$. We assumed that the off-diagonal cou-

pling is weak ($V^{10} = 0.1$) and that the two levels are coupled to optical phonons with narrow dispersion ($\sigma/\langle\omega\rangle$), i.e., we choose $\sigma = 0.1$. We performed calculation for the weak ($A = 2.0$) and strong ($A = 8.0$) diagonal coupling strength $A \equiv m\delta^2/2\hbar$ at low ($\beta^* = 4.0$), intermediate ($\beta^* = 1.0$) and high ($\beta^* = 0.25$) reduced temperature $\beta^* = \beta\hbar\langle\omega\rangle$.

In Fig. 1 we display semi-logarithmic plots of the FQ transition rate (data points) and semiclassical approxi-

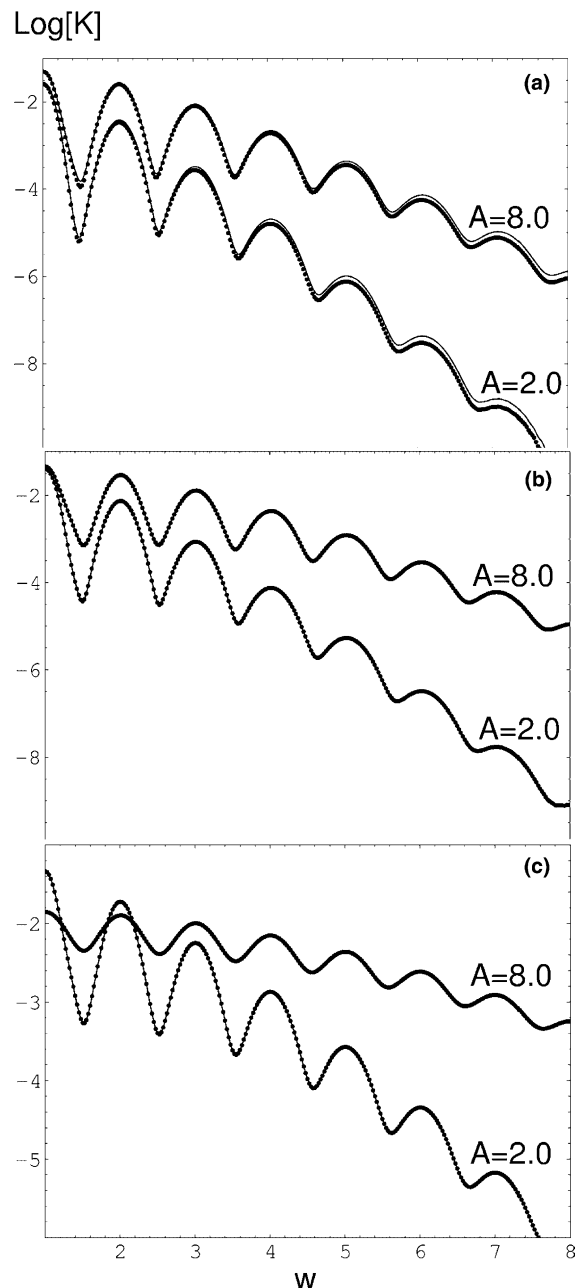


Fig. 1. Semi-log plots of the reduced two-level system transition rate K with static coupling vs the reduced energy gap w : FQ rate (data points) and mixed quantum-classical rate with quantum bath corrections (solid lines) are compared for low ($\beta^* = 4.0$, panel a), intermediate ($\beta^* = 1.0$, panel b) and high ($\beta^* = 0.25$, panel c) reduced temperature β^* for weak ($A = 2.0$) and strong ($A = 8.0$) diagonal coupling.

mation (solid lines) scaled by $\langle\omega\rangle$, i.e., $K = k_{1\rightarrow 0}/\langle\omega\rangle$ vs the reduced energy gap $w \equiv \omega_{el}/\langle\omega\rangle$. We see that this leading order semiclassical approximation shows an excellent agreement with FQ at intermediate and high temperature in the whole range of w and only slightly overestimates FQ at low temperature for large values of w (cf. Fig. 1 of [19]). This agreement is somewhat better for larger strength of coupling A (upper curves).

6. Concluding remarks

We have studied the dissipative dynamics in a two-level system linearly coupled to the thermal bath, with an emphasis on the important role played by quantum corrections in evaluation of non-adiabatic (NA) transition rates and pure dephasing. All degrees of freedom of the bath have been treated in the harmonic approximation. We have considered the case when the interaction of the two level system with the bath is both diagonal and off-diagonal. We assumed that the diagonal coupling is modeled by the set of displaced but undistorted bath modes. The off-diagonal coupling has been realized through the NA coupling of the two-level system to the momenta of the relevant modes.

We derived equations of motion for the reduced two-level system density matrix. The obtained Markovian equations are a good description of the dissipative dynamics in the relaxation time scale after the initial Zeno period has lapsed [24,25,36]. We have extracted and analyzed the full quantum (FQ) NA transition rate and the expression for pure dephasing. We have shown that for this case both the FQ NA transition rate and the pure dephasing kernel can be *manifestly* decomposed into a contribution from the average thermal excitations of bath modes plus the zero point energy contribution. The latter may affect the excited ($k_{1\rightarrow 0}^{qhc}/2k_{1\rightarrow 0}^{qm}$) and ground ($1/2(1 - k_{1\rightarrow 0}^{zpc}/k_{1\rightarrow 0}^{qm})$) state population due to the non-vanishing zero point energy contribution to the amplitude of NA coupling. Neglect of zero point energy contribution violates detailed balance and is inconsistent with dynamics. Zero point energy contribution is non-negligible at any *finite* temperature. An extracted zero point energy contribution to the pure dephasing kernel confirms the result previously obtained by Reichman et al. [17] that pure dephasing may occur at zero temperature.

The time evolution of populations of two levels is trivially exponential. However, the time evolution of coherences is less trivial. In the strong diagonal and weak off-diagonal coupling case, we have three time scales. For the times of the order of the inverse of the two level renormalized frequency $t \sim 1/\tilde{\omega}_{el}$, the evolution of phase coherence is unitary. Here, both diagonal and off-diagonal system-bath interactions contribute to

the frequency modulation. For times shorter than the relaxation time but longer than the inverse of the two-level system renormalized frequency ($1/\tilde{\omega}_{el} < t \ll 1/2k_{1\rightarrow 0}^{qm}$), energy dissipation is negligible and the two-level system phase coherence undergoes a pure dephasing ($\sim \exp[-t^2/\tau_{\text{deph}}^2]$), with a quadratic time dependence. Finally, at times of the order of the relaxation time, $t \sim 1/k_{1\rightarrow 0}^{qm}$, phase coherence decays exponentially, and the two-level system wave function evolves into a statistical mixture.

We have studied the quantum-classical correspondence in the context of NA transition rates with an emphasis on quantum bath correlation function. This function plays a twofold role. First, in the exponent of this function, the real part determines pure dephasing, whereas the imaginary part yields a diagonal frequency modulation to the two-level system renormalized frequency. Second, the time evolution of this function determines the dynamics of quantum coherence in variables of the bath. Taking the classical bath limit in the quantum correlation function, we arrive at a corresponding classical counterpart, i.e., a mixed quantum-classical rate. This reflects the quantum-classical correspondence principle. Comparing expressions for the FQ and mixed quantum-classical rates shows that the latter is missing the quantum correction factor incorporating the quantum features of the thermal bath ignored in a mixed quantum-classical evaluation of the NA transition rate. This fact was first noticed by Borgis and Staib [28], and has been used by Prezhdo and Rossky [6] to show decomposition of the quantum NA transition rate into its mixed quantum-classical counterpart and the quantum correction factor for the case where bath modes wave functions can be approximated by frozen Gaussians. In the present work, we have demonstrated that for the case when a thermal bath can be modeled by the set of harmonic oscillators, this decomposition is rigorous and that within a mixed quantum-classical treatment, quantum bath corrections to both the NA transition rate and the pure dephasing kernel *can* be readily evaluated. Hence, true quantum dynamics can be recovered from a well chosen mixed quantum-classical description for this important model.

Although in mixed quantum-classical propagation schemes the quantum nature of the environment is ignored, mixed quantum-classical simulation data may supply sufficient information to construct a semiclassical approximation to the quantum correlation function, an important ingredient in evaluating both the quantum NA transition rate and pure dephasing. We have presented a simple approach that offers a systematic way of evaluating the quantum harmonic bath corrections based on results of mixed quantum-classical simulation data. In our approach we utilized the high temperature (HT) semiclassical approximation

to the quantum correlation function (also known as the ACL) [19,35]).

The fact that in the HT (or ACL) approach, the time correlation function can be calculated using a classical MD propagation scheme by replacing the quantum averaging over the initial bath states with the classical average over the position and momentum of modes propagated with the arithmetic average of unperturbed Hamiltonians associated with the initial and final states of the two-level system, is not new [19,35]. A new element in our analysis is an analytical foundation for realization that the quantum bath corrections to semiclassical NA transition rates and pure dephasing kernels can be both rigorously defined and systematically evaluated in terms of *classical* quantities within the same semiclassical approximation.

In view of the above findings, one is motivated to perform a model calculation of NA transition rates based on the developed HT semiclassical method corrected with respect to quantum bath effects and assess its accuracy by direct comparison with results for the FQ rate [37].

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Appendix A. Derivation of the master equation

The total Hamiltonian acquires the following quantized form:

$$H = \{\hbar\omega_{el} + H_b\}|1\rangle\langle 1| + \{\Delta + H_b\}|0\rangle\langle 0| + \sum_j \{V_j^{01}(a_j^+ - a_j)|0\rangle\langle 1| + V_j^{10}(a_j^+ - a_j)|1\rangle\langle 0|\} \quad (\text{A.1})$$

We use the correlation diagrams accumulated in Fig. 2. Here straight lines correspond to the quantum subsystem, curved lines stand for the j th-bath mode. The direction of reading is denoted by arrows. If in the direction of reading the line of the j th mode converges (diverges) to that of the

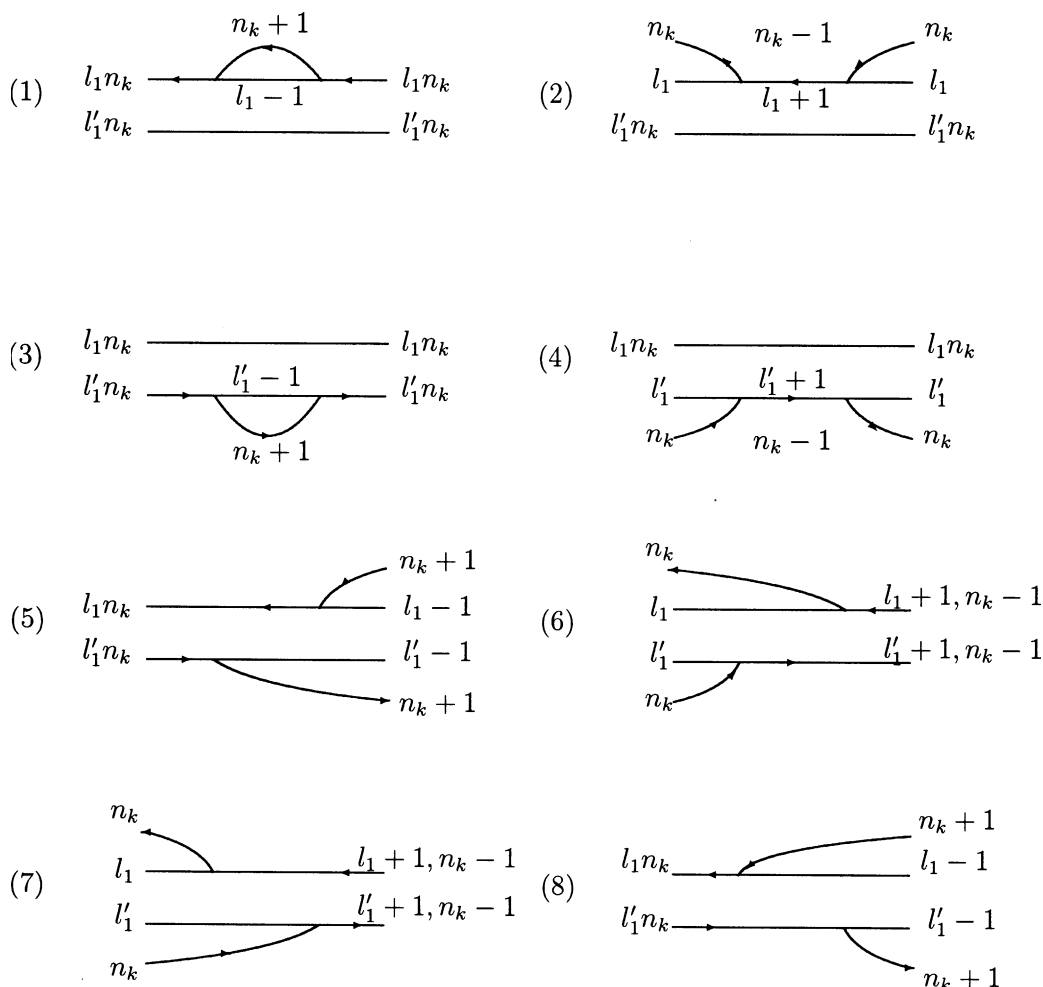


Fig. 2. The second order correlation space diagrams.

quantum system, then the mode of the bath loses (gains) a quantum of energy and the quantum system gains (loses) a quantum of energy. These processes are represented by vertices ($a_j|i\rangle\langle i+1|$ and $a_j^\dagger|i\rangle\langle i-1|$). The matrix element of the collision operator is

$$\begin{aligned} & \langle\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N | \theta^{(1)}(z) | l''_1, \{n''_j\}^N; l'''_1, \{n'''_j\}^N \rangle\rangle \\ &= \langle\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N | P^{(1)} L_0 P^{(1)} | l''_1, \{n''_j\}^N; l'''_1, \{n'''_j\}^N \rangle\rangle \\ &+ \langle\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N | P^{(1)} L_V Q^{(1)} \frac{1}{z - L_0} \\ &\times Q^{(1)} L_V P^{(1)} | l''_1, \{n''_j\}^N; l'''_1, \{n'''_j\}^N \rangle\rangle. \end{aligned} \quad (\text{A.2})$$

Using the unperturbed part of the Hamiltonian (A.1), we calculate a contribution from the L_0 -part ($H_c = H_b + \hbar\omega_{el}$, $H_g = H_b + \Delta$)

$$\begin{aligned} & \langle\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N | P^{(1)} [\{H_c|i\rangle\langle i+1| + H_g|i-1\rangle\langle i-1|] 1 - 1 \\ &\times \{H_c|i\rangle\langle i+1| + H_g|i-1\rangle\langle i-1|\} P^{(1)} | l''_1, \{n''_j\}^N; l'''_1, \{n'''_j\}^N \rangle\rangle \\ &= \hbar\omega_{el}(\delta_{l'_1, l_1-1} - \delta_{l'_1, l_1+1}) \\ &\times \delta_{l''_1, l_1} \delta_{l'''_1, l_1} \delta_{n''_k, n_k} \delta_{n'''_k, n'_k} + \Delta E, \end{aligned} \quad (\text{A.3})$$

where

$$\begin{aligned} \Delta E &= \langle\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N | [(H_b + \Delta) \times 1 \\ &- 1 \times H_b] \delta_{l'_1, l_1+1} + [H_b \times 1 \\ &- 1 \times (H_b + \Delta)] \delta_{l'_1, l_1-1} | l_1, \{n_j\}^N; l'_1, \{n'_j\}^N \rangle\rangle. \end{aligned} \quad (\text{A.4})$$

Now we calculate the L_V -part of the collision operator. We present calculation for diagram (1) in Fig. 1. The other diagrams can be calculated in a similar way. For the propagator we obtain

$$\begin{aligned} & \left\langle\left\langle l_1, \{n_j\}^N; l'_1, \{n'_j\}^N \left| \frac{1}{H_0 \times 1 - 1 \times H_0 - z} \right. \right. \right. \\ & \left. \left. \times l''_1, \{n''_j\}^N; l'''_1, \{n'''_j\}^N \right\rangle\right\rangle \rightarrow \frac{1}{\Delta E - \hbar\omega_{el} - i\epsilon}. \end{aligned} \quad (\text{A.5})$$

The vertices are

$$\begin{aligned} & \langle\langle l_1 - 1, n_j + 1, \{n_j\}^{N-1}; l'_1, n'_j, \{n'_j\}^{N-1} | a_j^\dagger | i - 1 \rangle\rangle \\ & \times \langle i | l_1, n_j, \{n_j\}^{N-1}; l'_1, n'_j, \{n'_j\}^{N-1} \rangle\rangle \\ &= (n_j + 1)^{1/2} e^{-i\omega_j t} \delta_{l'_1, l_1-1}^{Kr} \langle\{n_j\}^{N-1} | \{n'_j\}^{N-1}\rangle, \end{aligned} \quad (\text{A.6})$$

$$\begin{aligned} & \langle\langle l_1, n_j, \{n_j\}^{N-1}; l'_1, n'_j, \{n'_j\}^{N-1} | a_j | i \rangle\langle i + 1 | l_1 - 1, n_j + 1, \\ & \times \{n_j\}^{N-1}; l'_1, n'_j, \{n'_j\}^{N-1} \rangle\rangle \\ &= (n_j + 1)^{1/2} e^{-i\omega_j t} \delta_{l'_1, l_1+1}^{Kr} \langle\{n_j\}^{N-1} | \{n'_j\}^{N-1}\rangle, \end{aligned} \quad (\text{A.7})$$

where $\langle\{n_j\}^{N-1} | \{n'_j\}^{N-1}\rangle$ stands for the overlap of the remaining $N - 1$ bath modes wave functions. Calculation of vertices (A.6) and (A.7) can be generalized to the case of l -level quantum system coupled to the bath. We obtain the contribution from diagram (1):

$$\begin{aligned} & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 l_1(n_j + 1), \\ & \times \frac{1}{\Delta E - \hbar\omega_{el} - i\epsilon} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}). \end{aligned} \quad (\text{A.8})$$

Contributions to (L_V)-part of the collision operator from diagrams (2)–(8) are calculated similarly. We obtain:

$$\begin{aligned} (2) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 (n_j)_i (l_1 + 1) \\ & \times \frac{1}{\hbar\omega_{el} - \Delta E - i\epsilon} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (3) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 l'_1(n_j + 1), \\ & \times \frac{1}{\hbar\omega_{el} - \Delta E - i\epsilon} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (4) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 (n_j)_i (l'_1 + 1) \\ & \times \frac{1}{\Delta E - \hbar\omega_{el} - i\epsilon} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (5) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 (l_1 l'_1)^{\frac{1}{2}} \\ & \times (n_j + 1)_i \frac{1}{\hbar\omega_{el} - \Delta E - i\epsilon} \\ & \times \rho(l_1 - 1, n_j + 1; l'_1 - 1, n_j + 1; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (6) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 (n_j)_i \\ & \times [(l_1 + 1)(l'_1 + 1)]^{\frac{1}{2}} \frac{1}{\Delta E - \hbar\omega_{el} - i\epsilon} \\ & \times \rho(l_1 + 1, n_j - 1; l'_1 + 1, n_j - 1; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (7) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 (n_j)_i \\ & \times [(l_1 + 1)(l'_1 + 1)]^{\frac{1}{2}} \frac{1}{\hbar\omega_{el} - \Delta E - i\epsilon} \\ & \times \rho(l_1 + 1, n_j - 1; l'_1 + 1, n_j - 1; \{n_j\}^{N-1}), \end{aligned}$$

$$\begin{aligned} (8) : & \frac{1}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle\{n_j\}^{N-1} | \{m_j\}^{N-1}\rangle|^2 \\ & \times (l_1 l'_1)^{\frac{1}{2}} (n_j + 1)_i \frac{1}{\Delta E - \hbar\omega_{el} - i\epsilon} \\ & \times \rho(l_1 - 1, n_j + 1; l'_1 - 1, n_j + 1; \{n_j\}^{N-1}), \end{aligned} \quad (\text{A.9})$$

where $(n_j + 1)_i = (n_j + 1)_0 \exp[-i\omega_j t]$ and $(n_j)_i = (n_j)_0 \exp[i\omega_j t]$. We express the propagator in terms of the principal part and the delta function as

$$\frac{1}{x \pm i\epsilon} \rightarrow P\left(\frac{1}{x}\right) \mp \pi i \delta(x). \quad (\text{A.10})$$

Now we sum over contributions (A.8) and (A.9), add a contribution from the L_0 -part (A.2) and substitute the resulting expression into Eq. (18) of the main text. We obtain the master equation for the total density matrix of the l -level system and the bath ($l > 2$)

$$\begin{aligned} & \frac{\partial}{\partial t} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}, t) \\ &= -i \left\{ \left[\tilde{\omega}_{\text{el}} - 1 \times \frac{\Delta}{\hbar} \right] \delta_{l'_1, l_1-1} \right. \\ & \quad \left. - \left[\tilde{\omega}_{\text{el}} - \frac{\Delta}{\hbar} \times 1 \right] \delta_{l'_1, l_1+1} \right\} \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}) \\ & \quad + \frac{2\pi}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 \delta(\Delta E - \hbar\omega_{\text{el}}) \\ & \quad \times |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \\ & \quad \times \left\{ (l_1 l'_1)^{\frac{1}{2}} (n_j + 1)_t \rho(l_1 - 1, n_j + 1; \right. \\ & \quad \times l'_1 - 1, n_j + 1; \{n_j\}^{N-1}, t) \\ & \quad \left. - \frac{l_1 + l'_1}{2} (n_j + 1)_t \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}, t) \right. \\ & \quad \left. + ((l_1 + 1)(l'_1 + 1))^{\frac{1}{2}} (n_j)_t \right. \\ & \quad \times \rho(l_1 + 1, n_j - 1; l'_1 + 1, n_j - 1; \{n_j\}^{N-1}, t) \\ & \quad \left. - \frac{(l_1 + 1) + (l'_1 + 1)}{2} (n_j)_t \right. \\ & \quad \left. \times \rho(l_1, n_j; l'_1, n_j; \{n_j\}^{N-1}, t) \right\}, \quad (\text{A.11}) \end{aligned}$$

where $l' = l \pm 1$.

To get equations of motion for the reduced two-level system density matrix we need to project Eq. (A.11) onto the two-level sector by restricting interaction to those that are relevant for the two-level system. To obtain the equation for $\rho_s(1, 0, t)$, we set $l_1 = 1$ and $l'_1 = 0$ in (A.11) (here only diagrams (1) and (4) contribute). We obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \rho(1, n_j; 0, n_j; \{n_j\}^{N-1}; t) \\ &= -i \left\{ \tilde{\omega}_{\text{el}} - \frac{\Delta}{\hbar} \right\} \rho(1, n_j; 0, n_j; \{n_j\}^{N-1}; t) \\ & \quad - \frac{2\pi}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \delta(\Delta E - \hbar\omega_{\text{el}}) \\ & \quad \times \frac{1}{2} [(n_j + 1)_t + (n_j)_t] \rho(1, n_j; 0, n_j; \{n_j\}^{N-1}, t). \quad (\text{A.12}) \end{aligned}$$

After integrating and using the factorizability condition (20), we obtain Eq. (21) of the main text. Similarly, to obtain the equation for $\rho_s(1, 1, t)$, we set $l_1 = 1$ and $l'_1 = 1$ in Eq. (A.11) (only diagrams (1), (3), (5) and (8) contribute). We obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \rho(1, n_j; 1, n_j; \{n_j\}^{N-1}, t) \\ &= \frac{2\pi}{\hbar} \sum_{\{m_j\}} \sum_j |V_j^{10}|^2 |\langle \{n_j\}^{N-1} | \{m_j\}^{N-1} \rangle|^2 \delta(\Delta E - \hbar\omega_{\text{el}}) \\ & \quad \times \{ (n_j)_t - [(n_j + 1)_t + (n_j)_t] \rho(1, n_j; 1, n_j; \{n_j\}^{N-1}, t) \}. \quad (\text{A.13}) \end{aligned}$$

After integrating and using (20), we obtain Eq. (21) of the main text.

Appendix B. A classical bath limit

We use the coherent state representation of a harmonic oscillator [38,39]. A decomposition of the number eigenstates $|n\rangle$ in terms of the set of coherent states $\{|\alpha\rangle\}$ defined as

$$|\alpha\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left[-\frac{m\omega}{2\hbar}(q - q(t))^2 + \frac{i}{\hbar}p(t)(q - q(t)) + \frac{i}{\hbar}S(t)\right] \quad (\text{B.1})$$

is given by

$$|n\rangle = \sum_{\alpha} |\alpha\rangle \langle \alpha|n\rangle, \quad (\text{B.2})$$

where the expansion coefficients $\langle \alpha|n\rangle$ are

$$C_{\alpha,n} = \langle \alpha|n\rangle = \langle \alpha|0\rangle \frac{(\alpha^*)^n}{(n!)^{\frac{1}{2}}} = \frac{(\alpha^*)^n}{(n!)^{\frac{1}{2}}} e^{-\frac{1}{2}|\alpha|^2}. \quad (\text{B.3})$$

Here the complex number $\alpha \equiv (q + ip)/\sqrt{2\hbar} = |\alpha|e^{i\phi}$ is an eigenvalue of the annihilation operator acting on the coherent state $|\alpha\rangle$ as $a|\alpha\rangle = \alpha|\alpha\rangle$, and the modulus $|\alpha|$ is related to the mean excitation of the oscillator \bar{n} as $\bar{n} = \langle \alpha|a^\dagger a|\alpha\rangle / \langle \alpha|\alpha\rangle = |\alpha|^2$. The expansion coefficient $\langle \alpha|n\rangle$ determines a probability of finding an oscillator in the n th-level in the coherent state $|\alpha\rangle$, and is given by the Poisson distribution,

$$P_{n,\alpha} = |\langle n|\alpha\rangle|^2 = e^{-|\alpha|^2} \frac{|\alpha|^{2n}}{n!} = \frac{\bar{n}^n e^{-\bar{n}}}{n!}. \quad (\text{B.4})$$

The bath mode wave function overlap is given as

$$\langle n|n'\rangle = \sum_{\alpha\alpha'} e^{-\bar{n}_{\alpha\alpha'} + i\Delta\Phi_{\alpha\alpha'}} \frac{(\bar{n}_{\alpha})^{\frac{n}{2}} (\bar{n}'_{\alpha'})^{\frac{n'}{2}}}{(n!)^{\frac{1}{2}} (n'!)^{\frac{1}{2}}} \langle \alpha|\alpha'\rangle, \quad (\text{B.5})$$

where $\bar{n}_{\alpha\alpha'} = 1/2(|\alpha|^2 + |\alpha'|^2) = 1/2(\bar{n}_{\alpha} + \bar{n}'_{\alpha'})$, and $\Delta\Phi_{\alpha\alpha'} = n'\phi_{\alpha'} - n\phi_{\alpha}$ is the phase difference. The overlap of two coherent states $|\alpha\rangle$ and $|\alpha'\rangle$ is

$$\begin{aligned} \langle \alpha|\alpha'\rangle &= \exp\left[\frac{i}{\hbar}\Delta S(t) - \frac{m\omega}{\hbar}\Delta q(t)^2 - \frac{1}{\hbar m\omega}\Delta p(t)^2 \right. \\ & \quad \left. + \frac{2i}{\hbar}\Delta q(t)\bar{p}(t)\right], \quad (\text{B.6}) \end{aligned}$$

where ΔS is a difference in phases associated with the excited and ground state wave functions, and we have

introduced the relative displacements in position $\Delta q(t) = (q(t) - q'(t))/2$ and momentum $\Delta p(t) = (p(t) - p'(t))/2$, around their average values $\bar{q}(t) = (q(t) + q'(t))/2$ and $\bar{p}(t) = (p(t) + p'(t))/2$, respectively. In terms of relative and average variables the phase difference becomes

$$\begin{aligned} \Delta S(t') &\equiv S'(t') - S(t') \\ &= \int_0^{t'} dt \left\{ \frac{2}{m} \Delta p(t) \bar{p}(t) - 2m\omega^2 \Delta q(t) \bar{q}(t) + \Delta(t) \right\}, \end{aligned} \quad (\text{B.7})$$

where $\Delta(t)$ is given by Eq. (4) in the main text. Taking the classical limit ($\hbar \rightarrow 0$) in Eq. (B.6) and using (B.7), we obtain

$$\lim_{\hbar \rightarrow 0} \langle \alpha | \alpha' \rangle = \delta_{\alpha\alpha'} e^{\frac{i}{\hbar} \int_0^{t'} dt \Delta_{\alpha\alpha'}(t)}. \quad (\text{B.8})$$

Then, in the limit $\hbar \rightarrow 0$ a product of the Franck-Condon factors becomes

$$\begin{aligned} \lim_{\hbar \rightarrow 0} \langle \{n_j\} | \{n'_j\} \rangle &= \prod_j \sum_{\alpha\alpha'} e^{-\bar{n}_{\alpha,j} + i\Delta\Phi_{\alpha\alpha',j}} \\ &\quad \times \frac{(\bar{n}_{\alpha,j})^{\frac{n_j}{2}} (\bar{n}'_{\alpha',j})^{\frac{n'_j}{2}}}{(n_j!)^{\frac{1}{2}} (n'_j!)^{\frac{1}{2}}} \delta_{\alpha\alpha'} e^{\frac{i}{\hbar} \int_0^{t'} dt \Delta_{\alpha\alpha',j}(t)} \\ &= \prod_j \sum_{\alpha} P_{\alpha j} e^{\frac{i}{\hbar} \int_0^{t'} dt \Delta_{\alpha j}(t)} = e^{\frac{i}{\hbar} \int_0^{t'} dt \Delta(t)}. \end{aligned} \quad (\text{B.9})$$

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