

Quantum master equations and steady states for the ultrastrong-coupling limit and the strong-decoherence limit

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In the framework of the theory of open quantum systems, we derive quantum master equations for the ultrastrong system-bath coupling regime and, more generally, the strong-decoherence regime. In this regime, the strong decoherence is complemented by slow relaxation processes. We use a generalization of the Förster and modified Redfield perturbation theories known in the theory of excitation-energy transfer. Also, we show that the mean-force Gibbs state in the corresponding limits is stationary for the derived master equations.

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I. INTRODUCTION

The dynamics of quantum systems strongly coupled to the environment (bath) is an actively developing direction in the theory of open quantum systems, which has many applications in physics, especially in quantum thermodynamics [1–5]. Although the approximation of weak system-bath coupling is widely used and many classical results of the theory of open quantum systems have been obtained in the framework of this approximation (including celebrated Redfield and Davies quantum master equations [6–8]), this approximation is too restrictive in many physical systems.

If we cannot apply the weak-coupling approximation and the problem is not exactly solvable, then we have three possibilities: We can apply one of the numerically exact methods, such as the hierarchical equations of motion (HEOM) [9–11], an approximation of an infinite bath by a finite number of oscillation modes obeying Markovian dynamics (see Refs. [12] for a review and, e.g., Refs. [13–17] for recent results). The second possibility is to map the system into a transformed system (which includes some degrees of freedom of the bath) for which the weak-coupling approximation can be used. Examples are the collective coordinate method [4,18] and the polaron transformation approach [19,20]. The third possibility is to develop a perturbation theory different from the weak-coupling perturbation theory. Well-known examples are the singular-coupling limit [21–23] and the low-density limit [24–26].

The aim of this paper is to develop a perturbation theory for the ultrastrong-coupling limit, which is the opposite of the weak-coupling limit. There is an increasing interest in this regime in the last years [27–32]. Moreover, we argue that the ultrastrong-coupling limit can be considered to be a particular case of a more general approximation called the strong-decoherence limit.

We show that, in fact, the so-called Förster approximation from excitation energy transfer (EET) theory [33–37]

describes ultrastrong system-bath coupling. We generalize this approximation to the general setting of open quantum systems. The more general strong-decoherence limit also involves a generalization of the modified Redfield theory that is also widely used in the theory of EET.

The Förster theory [38,39] is the basic theory of EET and is based on the assumption that the couplings between the local excitations are much weaker than the system-bath coupling (which has the form of the local decoherence). This is the case of a strong system-bath coupling.

The modified Redfield approach [40] (in contrast with the weak-coupling or the standard Redfield approach) treats the pure decoherence part of the system-bath interaction nonperturbatively. In other words, only the off-diagonal part of the system-bath interaction Hamiltonian (in the eigenbasis of the isolated system Hamiltonian) is assumed to be small. This theory is also basic for understanding the coherent EET in biological light-harvesting complexes [35–37].

We adapt these approximations, which have proved to be very useful in the theory of EET, to the general framework of open quantum systems and also generalize and unify them. In particular, we allow the collective action of strong pure decoherence on subspaces of the system's Hilbert space and weak-coupling dynamics inside these subspaces. For example, a subspace may correspond to degenerate or nearly degenerate energy levels. This generalization is important since the modified Redfield theory is known to fail in this case [36,41,42]. Moreover, this is not a technical limitation but a fundamental limitation of the modified Redfield theory in its usual formulation (where the pure decoherence acts on different energy eigenstates separately, not collectively) [43].

Another motivation of this work is to derive the system steady state at the ultrastrong-coupling regime and the strong-decoherence regimes. This is of a particular importance due to a discussion in Refs. [27,28] about the correct form of the steady state for the ultrastrong-coupling regime. We show that the steady state corresponds to the so-called mean-force Gibbs state, which confirms the conjecture of Ref. [28]. We explain in which sense the state conjectured in Ref. [27] can be considered stationary. Note that the mean-force Gibbs state

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is the reduced density operator of the system corresponding to the “total” system-bath Gibbs state, see Ref. [44] for a review. It differs from the usual canonical Gibbs state with respect to the system Hamiltonian.

The paper is organized as follows: In Sec. II, we introduce the model: an arbitrary system with a purely discrete spectrum interacting with the thermal bosonic bath. In Sec. III, we consider a simple particular case of the ultrastrong-coupling (or strong-decoherence) approximation. It generalizes the Förster approximation and includes the nondegenerate ultrastrong interaction. We derive the corresponding master equation and its steady state. This master equation describes the dynamics of the populations (the diagonal elements of the density matrix) in the so-called pointer basis. The coherences are small (due to the strong-decoherence regime) but can also be calculated. This is done in Sec. IV. Using this, we derive corrections to the steady state conjectured in Ref. [28] and derived in the preceding Sec. III. In the end of Sec. IV, the range of validity of the described approximation is discussed. In Sec. V, we introduce the general form of the strong-decoherence approximation and derive the corresponding master equation and its steady state.

II. MODEL

Let us consider the Hamiltonian of an open quantum system,

$$H = H_S + H_B + H_I, \quad (1)$$

where three terms on the right-hand side are a free system Hamiltonian (corresponding to a Hilbert space \mathcal{H}_S), a free bath Hamiltonian (corresponding to a Hilbert space \mathcal{H}_B), and a system-bath interaction Hamiltonian, respectively. H_S is assumed to have a purely discrete spectrum. We consider the bath of free harmonic oscillators:

$$H_B = \int \omega(\xi) a(\xi)^\dagger a(\xi) d\xi, \quad (2)$$

where $\omega(\xi) \geq 0$ is the frequency of the mode ξ and $a(\xi)^\dagger$ and $a(\xi)$ are the creation and annihilation operators for the mode ξ . Let the interaction Hamiltonian take the form

$$H_I = \sum_{\alpha=1}^M A_\alpha \otimes B_\alpha, \quad (3)$$

where A_α are Hermitian operators on \mathcal{H}_S with purely discrete spectra and

$$B_\alpha = \int [\overline{d_\alpha(\xi)} a(\xi) + d_\alpha(\xi) a(\xi)^\dagger] d\xi. \quad (4)$$

We assume that the state of the bath is thermal with an inverse temperature β [not to be confused with the subindex β , which will be used as the second subindex in the double summations (3)]. The generalization to the case of several thermal baths with different temperatures is straightforward. Let us denote this state

$$\rho_B = Z^{-1} e^{-\beta H_B}, \quad Z = \text{Tr} e^{-\beta H_B}. \quad (5)$$

Note that, due to an infinite number of oscillation modes, strictly speaking, Z is ill-defined and ρ_B is not a genuine

density operator. To deal with such a bath state, we can either consider the limit of a large finite number of modes or treat ρ_B in the “generalized” sense as a functional on the algebra of canonical commutation relations according to the formula

$$\text{Tr}[\rho_B a^\dagger(\xi) a(\xi')] \equiv \langle a^\dagger(\xi) a(\xi') \rangle = n_{\text{BE}}[\omega(\xi)] \delta(\xi - \xi'),$$

and the Gaussian property. Here $n_{\text{BE}}(\omega) = (e^{\beta\omega} - 1)^{-1}$ is the Bose-Einstein distribution and $\langle \cdot \rangle$ denotes the expectation with respect to the thermal state. We can associate $\text{Tr} O \rho_B$ with $\langle O \rangle$ for an arbitrary bath observable O .

Reorganization Hamiltonian and boundedness from below

It is instructive to rewrite the Hamiltonian in the form

$$H = H_S - H_S^{(\text{reorg})} + H_{BI}, \quad (6)$$

where

$$H_{BI} = \int \omega(\xi) \tilde{a}(\xi)^\dagger \tilde{a}(\xi) d\xi \quad (7)$$

represents both the bath and its interaction with the system,

$$\tilde{a}(\xi) = a(\xi) + \sum_{\alpha=1}^M \frac{d_\alpha(\xi)}{\omega(\xi)} A_\alpha, \quad (8)$$

are system-dependent displaced ladder operators, and

$$H_S^{(\text{reorg})} = \sum_{\alpha, \beta=1}^M \left(\int \frac{\overline{d_\alpha(\xi)} d_\beta(\xi)}{\omega(\xi)} d\xi \right) A_\alpha A_\beta \quad (9)$$

is the reorganization Hamiltonian [28,33,34]. We see that H is bounded from below whenever H_S is bounded from below and A_α are bounded (in particular, if \mathcal{H}_S is finite-dimensional).

If some of A_α are unbounded, then H can be unbounded from below in the strong system-bath coupling case and, thus, without a thermodynamically stable (ground) state. To avoid this, the counter-term $H_S^{(\text{reorg})}$ should be added to the Hamiltonian:

$$\tilde{H} = H_S + H_{BI}. \quad (10)$$

This Hamiltonian is bounded from below whenever H_S is. In principle, Hamiltonian \tilde{H} is often more fundamental than H since the interaction between the system and the bath oscillators often manifests itself in system-dependent displacements of the oscillator equilibria. For example, this is so in the theory of EET [33–35,45]. Hamiltonian \tilde{H} can be rewritten in form (1) as

$$\tilde{H} = H_S + H_S^{(\text{reorg})} + H_B + H_I, \quad (11)$$

i.e., the reorganization Hamiltonian appears naturally and can be merged with H_S .

Since Hamiltonian (1) is widely used in the theory of open quantum systems, we start from this form to make results suitable to use within the standard setting. We assume that this does not produce pathologies. For example, for simplicity, we can assume that \mathcal{H}_S is finite dimensional. Or we can assume that H_S already includes the reorganization term. If we start from Hamiltonian (10), then it is easy to modify all subsequent derivations accordingly.

III. NONDEGENERATE ULTRASTRONG COUPLING

A. Description of the approximation

Let us assume that all A_α in (3) commute and, thus, are simultaneously diagonalizable in a common eigenbasis $\{|n\rangle\}$:

$$A_\alpha = \sum_n \theta_{\alpha n} |n\rangle \langle n|. \quad (12)$$

For simplicity, in this section, we additionally assume that:

(1) For each n , there exists α such that $\theta_{\alpha n} \neq 0$ (i.e., there is no subspace which does not interact with the bath).

(2) Only the zero eigenvalue of each A_α may be degenerate. In other words, if $\theta_{\alpha n} = \theta_{\alpha m}$, then $\theta_{\alpha n} = \theta_{\alpha m} = 0$.

If these two conditions are met, the basis $|n\rangle$ is uniquely defined.

Then, the system Hamiltonian H_S can be expressed as

$$H_S = \sum_n \varepsilon_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|, \quad (13)$$

where ε_n are real and $J_{nm}^* = J_{mn}$.

Let us assume that J_{nm} can be treated as small with respect to the system-bath coupling strength. Note that, in the theory of the weak-coupling limit, the interaction Hamiltonian H_I is treated as a small perturbation. Here we consider the situation where

$$V = \sum_{n \neq m} J_{nm} |n\rangle \langle m| \quad (14)$$

can be treated as a small perturbation, while the rest of the Hamiltonian (1) (which includes H_I) is not small:

$$H_0 = \sum_n \varepsilon_n |n\rangle \langle n| + H_B + H_I. \quad (15)$$

Since H_I can be arbitrarily large, this case includes the ultrastrong-coupling limit. We refer to this case as the “strong-decoherence limit” because the unperturbed dynamics corresponds to decoherence in the basis $\{|n\rangle\}$.

In the theory of the weak-coupling limit, the relaxation occurs in the eigenbasis of H_S . In contrast, here, it occurs in the common eigenbasis of A_α . In the context of EET theory, this is the local excitation basis (see Remark 3 below), while, in the context of measurement theory and decoherence theory, it is called the pointer basis [27,46].

Also note that interaction (12) without a small correction V (i.e., the case of pure decoherence, when $\{|n\rangle\}$ is an eigenbasis of both all A_α and H_S) was considered in recent papers [47,48].

Remark 1. Although we treat V as a small perturbation, actually, it is not assumed that J_{nm} are smaller than ε_n . It is only assumed that J_{nm} are much smaller than $\theta_{\alpha n}$, which ensures strong decoherence. A detailed analysis will be given in Sec. IV C.

Remark 2. Note that the “literal” ultrastrong-coupling limit

$$H = H_S + H_B + \lambda^{-1} H_I, \quad \lambda \rightarrow 0, \quad (16)$$

seems to lead to a less precise theory. In this case, we rescale the time as $t \mapsto \lambda t$, which is equivalent to the scaling of the Hamiltonian:

$$H \mapsto \lambda H = \lambda(H_S + H_B) + H_I, \quad (17)$$

which means that we treat all the parameters of H_S and H_B , e.g., the differences between the energies, $\varepsilon_n - \varepsilon_m$, as small. However, as we will see, these energy differences will play an important role in the final formulas. In the perturbation theory described only V is treated as small, which leads to a more precise theory. So, the proposed perturbation theory with respect to V is the right formalization of the ultrastrong-coupling regime.

Remark 3. In the theory of EET, a state $|n\rangle$ corresponds to the excitation of the local site (molecule) n , ε_n are local excitation energies, and J_{nm} are the dipole couplings between the molecules. Usually, it is assumed that each molecule is coupled to its own phonon bath. In this case $\theta_{\alpha n} = \delta_{\alpha n}$ (here δ is the Kronecker symbol) and

$$d_\alpha(\xi) d_\beta(\xi) \equiv 0 \quad (18)$$

for $\alpha \neq \beta$. Equation (18) means that each mode may interact with at most one site. A violation of Eq. (18) corresponds to correlated baths, which are also considered in the theory of EET [49]. Then, the described approximation is known as the Förster approximation [33–35,38,39]. Here we adapt it to a general context of open quantum systems and, in Sec. V, allow more general system-bath interactions.

B. Projection operator

The complicated joint dynamics of the system and the bath can be reduced to a simplified quantum master equation for a finite number of “slow” degrees of freedom only if the other (“fast”) degrees of freedom quickly relax to a state depending on the slow degrees of freedom. This is typically formalized in the language of projection operators [26,33,34,50]. Let \mathcal{P} be a projection operator acting on the space of joint system-bath trace-class operators \mathcal{S} , and we assume that the joint system-bath state $\rho(t)$ quickly relaxes to the subspace $\mathcal{S}_0 = \mathcal{P}\mathcal{S}$. This operator should agree with the decomposition of the Hamiltonian into a reference part and a small perturbation [see Eq. (90) below]. Namely, the subspace \mathcal{S}_0 should be invariant with respect to the “fast” unitary dynamics $e^{-it\mathcal{L}_0}$, where $\mathcal{L}_0 = [H_0, \cdot]$.

Let us analyze the fast dynamics $e^{-it\mathcal{L}_0}$. Due to the strong decoherence, an off-diagonal part of ρ [in the basis $\{|n\rangle\}$] vanishes (this is true under some conditions on the spectral densities, see the end of Sec. III E). So, $\mathcal{S}_0 = \sum_n \mathcal{S}^{(n)}$, where $\mathcal{S}^{(n)} = \Pi_n \mathcal{S} \Pi_n$, $\Pi_n = |n\rangle \langle n|$.

Also, we can see that the fast dynamics in the subspaces $\mathcal{S}^{(n)}$ are decoupled from each other:

$$H_0 = \sum_n \Pi_n H_0^{(n)} \Pi_n, \quad (19)$$

where

$$H_0^{(n)} = \varepsilon_n + H_B + \sum_\alpha \theta_{\alpha n} B_\alpha. \quad (20)$$

So, it suffices to describe the fast dynamics inside each subspace. Moreover, as we see, the dynamics inside each subspace is reduced to the bath dynamics: The dynamics of the system is trivial. Let us express the bath Hamiltonian for each subspace as a Hamiltonian of displaced harmonic oscillators:

$$H_0^{(n)} = \varepsilon_n - \delta\varepsilon_n + H_B^{(n)}, \quad (21)$$

where

$$H_B^{(n)} = \int \omega(\xi) a_n(\xi)^\dagger a_n(\xi) d\xi, \quad (22)$$

$$a_n(\xi) = a(\xi) + \frac{d_n(\xi)}{\omega(\xi)}, \quad (23)$$

$$d_n(\xi) = \sum_{\alpha=1}^M \theta_{\alpha n} d_\alpha(\xi), \quad (24)$$

$$\delta\varepsilon_n = \int \frac{|d_n(\xi)|^2}{\omega(\xi)} d\xi. \quad (25)$$

The quantities $\delta\varepsilon_n$ are called the reorganization energies [33,34]. Often, they are considered to be parameters characterizing the system-bath coupling strength. The minus sign in Eq. (21) is caused by the absence of the reorganization part in the original Hamiltonian (1), see the discussion in Sec. II A and especially Eq. (6). If we had originally postulated the Hamiltonian (11) with the reorganization part, we would have obtained simply $\varepsilon_n + H_B^{(n)}$ on the right-hand side of (21), i.e., simply the original “bare” energy.

Under the free dynamics, the bath state quickly thermalizes, hence $\rho^{(n)} \in \mathcal{S}^{(n)}$ quickly relaxes to the state of the form $\rho_S^{(n)} \otimes \rho_B^{(n)}$, where $\rho_B^{(n)} = Z^{-1} e^{-\beta H_B^{(n)}}$ is the thermal state with respect to the Hamiltonian $H_B^{(n)}$ of the displaced oscillators. Also, $\rho_S = \text{Tr}_B \rho$ is the reduced system operator and $\rho_S^{(n)} = \Pi_n \rho_S \Pi_n$.

Remark 4. The conjecture of the thermalization of the bath under the free dynamics is also used in the theory of weak coupling. Namely, the Born approximation states that the joint system-bath state is always close to a product state $\rho_S(t) \otimes \rho_B$. The corresponding projection operator used in the weak-coupling theory is $\mathcal{P}\rho = (\text{Tr}_B \rho) \otimes \rho_B$. This is a formalization of the assumption that the free dynamics quickly turns a bath state into the thermal state ρ_B uncoupled from the system. Here we have exactly the same assumption, with the only difference of an n -dependent (system-dependent) displacement. Of course, such thermalization under unitary dynamics can take place only in a weak sense (i.e., in terms of averages of local and quasilocal observables), see rigorous results in Refs. [51,52].

Thus, we can define the projection operator \mathcal{P} as follows:

$$\mathcal{P}\rho = \sum_n \Pi_n (\text{Tr}_B \rho) \Pi_n \otimes \rho_B^{(n)} \quad (26)$$

$$= \sum_n p_n |n\rangle \langle n| \otimes \rho_B^{(n)}, \quad (27)$$

where $p_n = \langle n | \text{Tr}_B \rho | n \rangle$.

The slow dynamics consists of transitions between different subspaces $\mathcal{S}^{(n)}$ governed by the perturbation V . Fast and slow dynamics are schematically represented in Fig. 1.

Note that somewhat similar types of the projection operators and the corresponding master equations were considered in Refs. [53–57]. In our approach, the bath equilibrium state depends on the system subspace. In these works, the bath (rather than the system) is decomposed into a sum of subspaces which determine different dynamics for the system.

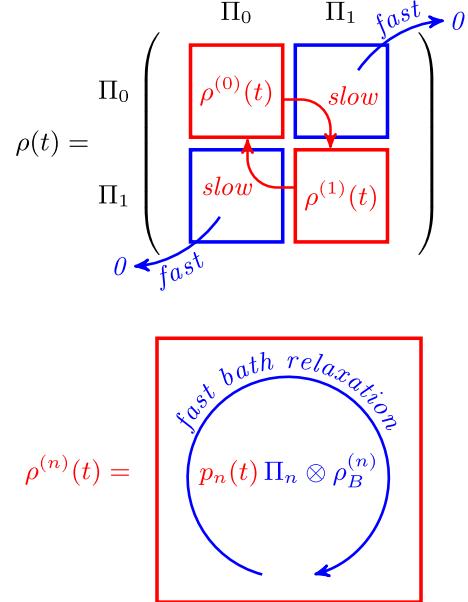


FIG. 1. Fast and slow processes at the nondegenerate ultrastrong coupling. For simplicity, here, the system is two dimensional. The blue color denotes the fast processes and degrees of freedom and the red color denotes the slow ones. The slow processes are described by a quantum master equation. The notations are as in the text: $\Pi_n = |n\rangle \langle n|$, $\rho_B^{(n)}$ are displaced bath thermal equilibrium states, and $p_n(t)$ are populations of the states $|n\rangle$. The bottom part of the figure depicts the red squares [corresponding to $\rho^{(n)}(t) = \Pi_n \rho(t) \Pi_n$] in more detail. The fast processes are the decoherence (reduction to zero of the off-diagonal blocks) and the bath relaxation, while the slow process is the relaxation of the populations.

C. Master equation

Denote $\mathcal{L} = [H, \cdot]$, $\mathcal{L}_0 = [H_0, \cdot]$, and $\mathcal{L}' = [V, \cdot]$. We work in the interaction picture with respect to H_0 and denote $\rho(t) = e^{i\mathcal{L}_0 t} e^{-i\mathcal{L}_0 t} \rho_0$,

$$V(t) = e^{i\mathcal{L}_0 t} V = \sum_{n \neq m} J_{nm} e^{i(\bar{\varepsilon}_n - \bar{\varepsilon}_m)t} e^{iH_B^{(n)} t} |n\rangle \langle m| e^{-iH_B^{(m)} t}, \quad (28)$$

and $\mathcal{L}'(t) = [V(t), \cdot] = e^{i\mathcal{L}_0 t} \mathcal{L}' e^{-i\mathcal{L}_0 t}$. Here,

$$\bar{\varepsilon}_n = \varepsilon_n - \delta\varepsilon_n.$$

We assume that $\rho(0) = \mathcal{P}\rho(0)$. Since $\mathcal{P}\mathcal{L}'(t)\mathcal{P} = 0$, the standard derivation of the Markovian second-order master equation [26,33,50] (see also Appendix A) leads to

$$\mathcal{P}\dot{\rho}(t) = \int_0^\infty d\tau \mathcal{P}\mathcal{L}'(t)\mathcal{L}'(t-\tau)\mathcal{P}\rho(t). \quad (29)$$

Since, in our case,

$$\mathcal{P}\mathcal{L}_0 = \mathcal{L}_0\mathcal{P} = 0, \quad (30)$$

Eq. (29) can be rewritten as

$$\mathcal{P}\dot{\rho}(t) = \int_0^\infty d\tau \mathcal{P}\mathcal{L}'(\tau)\mathcal{L}'\mathcal{P}\rho(t). \quad (31)$$

Substituting expression (27) for $\mathcal{P}\rho$, we obtain

$$\dot{p}_n(t) = \sum_{m \neq n} [\gamma_{nm} p_m(t) - \gamma_{mn} p_n(t)], \quad (32)$$

where

$$\begin{aligned} \gamma_{nm} &= 2|J_{nm}|^2 \operatorname{Re} \int_0^\infty d\tau e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \langle e^{iH_B^{(m)}\tau} e^{-iH_B^{(n)}\tau} \rangle_m \\ &= |J_{nm}|^2 \int_{-\infty}^{+\infty} d\tau e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \langle e^{iH_B^{(m)}\tau} e^{-iH_B^{(n)}\tau} \rangle_m, \end{aligned} \quad (33)$$

and $\langle O \rangle_m = \operatorname{Tr}_B O \rho_B^{(m)}$. So, since the off-diagonal part of $\rho_S(t) = \operatorname{Tr}_B \rho(t)$ quickly vanishes, the master equations describes only the diagonal elements $p_n(t)$.

D. Mean-force Gibbs steady state

An explicit expression of γ_{mn} will be obtained in the next section, but, even the general expression (33) allows us to derive the steady state. Let us change the variable of integration in Eq. (33) by $s = -\tau - i\beta$:

$$\begin{aligned} \gamma_{nm} &= |J_{nm}|^2 \int_{-\infty}^{+\infty} ds e^{-i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)(s+i\beta)} \\ &\quad \times \langle e^{-iH_B^{(m)}(s+i\beta)} e^{iH_B^{(n)}(s+i\beta)} \rangle_m \\ &= e^{\beta(\bar{\varepsilon}_m - \bar{\varepsilon}_n)} |J_{nm}|^2 \int_{-\infty}^{+\infty} ds e^{i(\bar{\varepsilon}_n - \bar{\varepsilon}_m)s} \\ &\quad \times \langle e^{-iH_B^{(m)}s} e^{iH_B^{(n)}s} e^{-\beta H_B^{(n)}} e^{\beta H_B^{(m)}} \rangle_m \\ &= e^{\beta(\bar{\varepsilon}_m - \bar{\varepsilon}_n)} \gamma_{mn}, \end{aligned} \quad (34)$$

where we have used

$$\langle O e^{-\beta H_B^{(n)}} e^{\beta H_B^{(m)}} \rangle_m = \langle O \rangle_n. \quad (35)$$

We have obtained the detailed balance conditions. Then, the following populations and the corresponding density operator are stationary:

$$p_n^{(\text{st})} = Z_S^{-1} e^{-\beta \bar{\varepsilon}_n}, \quad (36)$$

where

$$Z_S = \sum_m e^{-\beta \bar{\varepsilon}_m} = \operatorname{Tr} e^{-\beta \sum_n \Pi_n \bar{H}_S \Pi_n}, \quad (37)$$

or, equivalently,

$$\rho_S^{(\text{st})} = Z_S^{-1} e^{-\beta \sum_n \Pi_n \bar{H}_S^{(\text{d})} \Pi_n}. \quad (38)$$

Here,

$$\bar{H}_S^{(\text{d})} = \sum_n \bar{\varepsilon}_n |n\rangle \langle n| \quad (39)$$

is the “renormalized” diagonal part of the system Hamiltonian.

It is believed that, if the system is ergodic, i.e., there is no nontrivial proper subspace of the system’s Hilbert space \mathcal{H}_S , which is invariant with respect to the system-bath dynamics, then the reduced state of the system converges to the so-called mean-force Gibbs (MFG) state

$$\rho_S^{(\text{MFG})} = \frac{\operatorname{Tr}_B e^{-\beta H}}{\operatorname{Tr} e^{-\beta H}} \quad (40)$$

(i.e., the reduced density operator of the system corresponding to the “total” Gibbs state of the whole system + bath complex) [44]. State (38), obviously, coincides with the mean-force Gibbs state in the considered limit (small J_{nm}). Also, it coincides with the mean-force Gibbs state calculated for the “literal” ultrastrong-coupling limit (16) [28].

Remark 5. Note that, in the “literal” ultrastrong-coupling limit, the reorganization energy (25) tends to infinity and the counterterm discussed in Sec. II A is obligatory. A small difference with the result of Ref. [28] is caused by this difference: We have not introduced this counter-term to the original Hamiltonian (1). We could do so to obtain exactly the same result.

If the system is ergodic, i.e., there is no nontrivial proper subspace of states $\{|n\rangle\}$ isolated from the other states, than stationary state (38) is unique.

Not that a mathematically rigorous proof of convergence to the state (38) for the spin-boson model and super-Ohmic spectral densities [see Eq. (47) and the first equality in Eq. (54) below] such that $\mathcal{J}(\omega) = O(\omega^3)$ as $\omega \rightarrow 0$ has been given in Refs. [58,59]. Here, we give a “physically rigorous” proof, i.e., not mathematically rigorous, but, nevertheless, based on the microscopic model and physically plausible assumptions.

E. Rate constants

To calculate the rate constants γ_{nm} , we should obtain an explicit expression for $\langle e^{iH_B^{(m)}t} e^{-iH_B^{(n)}t} \rangle_m$. It turns out that (see Appendix B)

$$\begin{aligned} \langle e^{iH_B^{(m)}t} e^{-iH_B^{(n)}t} \rangle_m &\equiv \zeta_{nm}(t) \\ &= \exp \left[- \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m})(g_{\alpha\beta}(t) \right. \\ &\quad \left. + it\delta\varepsilon_{\alpha\beta}) \right], \end{aligned} \quad (41)$$

where

$$\delta\varepsilon_{\alpha\beta} = \int \frac{\overline{d_\alpha(\xi)} d_\beta(\xi)}{\omega(\xi)} d\xi, \quad (42)$$

and

$$g_{\alpha\beta}(t) = \int_0^t ds_1 \int_0^{s_1} ds_2 C_{\alpha\beta}(s_2). \quad (43)$$

Here,

$$C_{\alpha\beta}(t) = \langle e^{iH_B t} B_\alpha e^{-iH_B t} B_\beta \rangle \quad (44)$$

are the bath correlation functions. Recall that $\langle O \rangle = \operatorname{Tr}_B O \rho_B$ and $\rho_B = Z^{-1} e^{-\beta H_B}$. In spectroscopy, $g_{\alpha\beta}(t)$ are called the lineshape functions since the absorption and fluorescence spectra are expressed through them. We assume that the bath correlation functions $C_{\alpha\beta}(t)$ are integrable. Then the functions $g_{\alpha\beta}(t)$ grow linearly with t for large t .

It is worthwhile to note that $\gamma_{nm} \rightarrow 0$ in both the considered limit of small J_{nm} and the “literal” ultrastrong-coupling limit $\theta_{\alpha n} \rightarrow \infty$ (for all α and n), which was expected in view of the quantum Zeno effect. Slow dynamics of populations is a correction to the quantum Zeno effect.

Note also that

$$C_{\alpha\beta}^*(t) = C_{\beta\alpha}(-t), \quad (45a)$$

$$g_{\alpha\beta}^*(t) = g_{\beta\alpha}(-t), \quad (45b)$$

$$\zeta_{nm}^*(t) = \zeta_{nm}(-t), \quad (45c)$$

$$C_{\alpha\beta}(t) = \int d\xi \{ \overline{d_\alpha(\xi)} d_\beta(\xi) (n_{\text{BE}}[\omega(\xi)] + 1) e^{-i\omega(\xi)t} \\ + d_\alpha(\xi) \overline{d_\beta(\xi)} n_{\text{BE}}[\omega(\xi)] e^{i\omega(\xi)t} \}. \quad (46)$$

If we introduce the spectral densities

$$\mathcal{J}_{\alpha\beta}(\omega) = \int \overline{d_\alpha(\xi)} d_\beta(\xi) \delta[\omega(\xi) - \omega] d\xi, \quad (47)$$

then the bath correlation functions and the lineshape functions can be expressed as

$$C_{\alpha\beta}(t) = \int_0^\infty d\omega \{ \mathcal{J}_{\alpha\beta}(\omega) [n_{\text{BE}}(\omega) + 1] e^{-i\omega t} \\ + \mathcal{J}_{\beta\alpha}(\omega) n_{\text{BE}}(\omega) e^{i\omega t} \} \quad (48)$$

and

$$g_{\alpha\beta}(t) = - \int_0^\infty d\omega \left\{ \frac{\mathcal{J}_{\alpha\beta}(\omega)}{\omega^2} [n_{\text{BE}}(\omega) + 1] (e^{-i\omega t} + i\omega t - 1) \\ + \frac{\mathcal{J}_{\beta\alpha}(\omega)}{\omega^2} n_{\text{BE}}(\omega) (e^{i\omega t} - i\omega t - 1) \right\}. \quad (49)$$

We assume that the spectral densities are well defined and integrable. Furthermore, we assume that the limits $\lim_{\omega \rightarrow +0} \mathcal{J}_{\alpha\beta}(\omega)/\omega^2$ are non-zero (possibly infinite). This ensures the full fast decoherence in the basis $\{|n\rangle\}$ discussed in Sec. III B, see, e.g., Ref. [58].

F. Example: Spin-boson model at ultrastrong coupling

Let us consider the spin-boson model as an example. Let the system Hamiltonian be

$$H_S = \varepsilon \sigma_z = \varepsilon (|1\rangle \langle 1| - |0\rangle \langle 0|). \quad (50)$$

Let the system interact ultrastrongly with a single thermal bath with the inverse temperature β and the interaction Hamiltonian

$$H_I = \sigma_x \otimes B = (|+\rangle \langle +| - |-\rangle \langle -|) \otimes B, \quad (51)$$

where $|\pm\rangle = (|1\rangle \pm |0\rangle)/\sqrt{2}$, σ_z and σ_x are the Pauli matrices, and

$$B = \int [\overline{d(\xi)} a(\xi) + d(\xi) a(\xi)^\dagger] d\xi \quad (52)$$

[i.e., the sum (3) contains only one term and the subindices α and β disappear everywhere].

In the weak-coupling regime, relaxation occurs in the eigenbasis $\{|0\rangle, |1\rangle\}$ of σ_z . In the ultrastrong-coupling regime, it occurs in the eigenbasis $\{|+\rangle, |-\rangle\}$ of σ_x . So, $n \in \{+, -\}$, $\theta_\pm = \pm 1$. Let us express the H_S Hamiltonian in this basis:

$$H_S = \varepsilon (|+\rangle \langle -| + |-\rangle \langle +|), \quad (53)$$

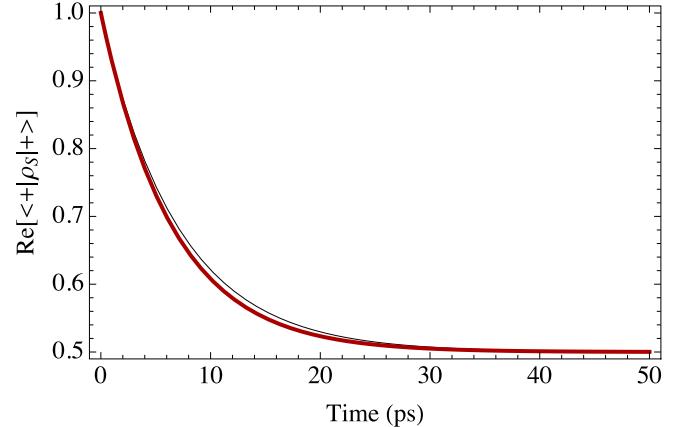


FIG. 2. Spin-boson model at ultrastrong coupling: performance of the master equation (32) (thick red line) in comparison with the numerically exact (but much more computationally expensive) method of HEOM (thin black line).

hence $\varepsilon_+ = \varepsilon_- = 0$ and $J_{-+} = J_{+-} = \varepsilon$. The application of the general formula (41) gives

$$\langle e^{iH_B^{(+)}t} e^{-iH_B^{(-)}t} \rangle_+ = \langle e^{iH_B^{(-)}t} e^{-iH_B^{(+)}t} \rangle_- = e^{-4[g(t)+it\delta\varepsilon]}.$$

For the simulation, we choose the Drude-Lorentz spectral density:

$$\mathcal{J}(\omega) \equiv \int |d(\xi)|^2 \delta(\omega(\xi) - \omega) dk = \frac{2\eta\Omega\omega}{\pi(\omega^2 + \Omega^2)} \quad (54)$$

with $\eta = 100 \text{ cm}^{-1}$ and $\Omega^{-1} = 100 \text{ fs}$ ($\Omega \approx 53.08 \text{ cm}^{-1}$). The temperature of the bath is $T = 300 \text{ K}$. The parameter ε is $\varepsilon = 10 \text{ cm}^{-1}$. The reorganization energy can be calculated as

$$\delta\varepsilon = \int_0^\infty \frac{\mathcal{J}(\omega)}{\omega} d\omega = \eta. \quad (55)$$

The bath correlation function can be expressed as

$$C(t) = \langle e^{iH_B t} B e^{-iH_B t} B \rangle \\ = \int_0^\infty \mathcal{J}(\omega) \left[\coth\left(\frac{\beta\omega}{2}\right) \cos\omega t - i \sin\omega t \right] d\omega. \quad (56)$$

We adopt the high-temperature approximation $\beta\Omega \ll 1$. For example, for the value used of $\Omega \approx 53.08 \text{ cm}^{-1}$ and the temperature $T = 300 \text{ K}$, we have $\beta\Omega \approx 0.24$. We have used that $\beta = 1/k_B T$, where $k_B \approx 0.734 \text{ cm}^{-1}/\text{K}$ is the Boltzmann constant. In this case, $\coth(\beta\omega/2)$ in Eq. (56) can be approximated as $2/(\beta\omega)$ and

$$C(t) \approx \eta\Omega \left(\frac{2}{\beta\Omega} - i \right) e^{-\Omega t}, \quad (57)$$

$$g(t) \approx \frac{\eta}{\Omega} \left(\frac{2}{\beta\Omega} - i \right) (e^{-\Omega t} + \Omega t - 1). \quad (58)$$

For our parameters, $\gamma_{+-} = \gamma_{-+} \approx 0.41 \text{ cm}^{-1}$ or 0.077 ps^{-1} , so the characteristic relaxation time is $(2\gamma_{+-})^{-1} \approx 6.5 \text{ ps}$. In Fig. 2, we compare the solution using master equation (32) with the numerically exact (but much more computationally expensive) method of hierarchical equations of motion (HEOM) in the high-temperature

approximation [10]. The initial state is

$$\rho(0) = |+\rangle\langle+| \otimes \rho_B. \quad (59)$$

We see almost ideal agreement.

IV. DYNAMICS OF COHERENCES

A. Corrections to the diagonal steady state

We have determined the populations, i.e., the diagonal matrix elements of the system density operator in the pointer basis $\{|n\rangle\}$. The projection operator \mathcal{P} projects onto the diagonal states. Hence, to obtain the off-diagonal elements (coherences), one needs the part $\mathcal{Q}\rho(t)$, where $\mathcal{Q} = 1 - \mathcal{P}$ [43]. If we denote

$$\rho_{nm}(t) = \langle n|\text{Tr}_B\{e^{-iH_0 t}\rho(t)e^{iH_0 t}\}|m\rangle, \quad (60)$$

$n \neq m$ (i.e., the coherences in the Schrödinger picture), then, assuming again $\rho(0) = \mathcal{P}\rho(0)$ and using Eq. (A5) for $\mathcal{Q}\rho(t)$, we obtain

$$\begin{aligned} \rho_{nm}(t) &= \langle n|\text{Tr}_B\{e^{-iH_0 t}[\mathcal{Q}\rho(t)]e^{iH_0 t}\}|m\rangle \\ &= -i \int_0^t d\tau \langle n|\text{Tr}_B\{e^{-iH_0 t}\mathcal{L}'(t-\tau)\mathcal{P}\rho(t-\tau)e^{iH_0 t}\}|m\rangle. \end{aligned} \quad (61)$$

Using $[\mathcal{P}\rho(t), H_0] = 0$ and Eq. (28), we obtain

$$\begin{aligned} \rho_{nm}(t) &= -i \int_0^t d\tau \langle n|\text{Tr}_B\{\mathcal{L}'(-\tau)\mathcal{P}\rho(t-\tau)\}|m\rangle \\ &= iJ_{nm} \int_0^t d\tau p_n(t-\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \langle e^{iH_B^{(m)}\tau} e^{-iH_B^{(n)}\tau} \rangle_n \\ &\quad - iJ_{nm} \int_0^t d\tau p_m(t-\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \langle e^{iH_B^{(m)}\tau} e^{-iH_B^{(n)}\tau} \rangle_m. \end{aligned}$$

Here, the integrands have been already calculated in Eq. (41). We can again [like in the derivation of Eq. (29)] apply the Markovian approximation and replace $p_n(t-\tau)$ and $p_m(t-\tau)$ by $p_n(t)$ and $p_m(t)$ since they evolve on larger timescales than the decay of the integrands. Thus, finally, we obtain

$$\begin{aligned} \rho_{nm}(t) &= iJ_{nm} p_n(t) \int_0^t \zeta_{mn}^*(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau \\ &\quad - iJ_{nm} p_m(t) \int_0^t \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau. \end{aligned} \quad (62)$$

For large times, we can extend the upper limit of integration in Eq. (62) to infinity and obtain constant coefficients after the populations. So, for large times, the dynamics of the coherences is driven by the populations. If we take the limit $t \rightarrow \infty$ and substitute the time-dependent populations $p_n(t)$ by their stationary values (36), then we obtain the steady-state coherences as the first-order corrections to the diagonal steady state (38):

$$\begin{aligned} \rho_{nm}^{(\text{st})} &= iJ_{nm} p_n^{(\text{st})} \int_0^\infty \zeta_{mn}^*(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau \\ &\quad - iJ_{nm} p_m^{(\text{st})} \int_0^\infty \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau. \end{aligned} \quad (63)$$

Since

$$\text{Re} \int_0^\infty \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau = \frac{1}{2} \int_{-\infty}^{+\infty} \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau,$$

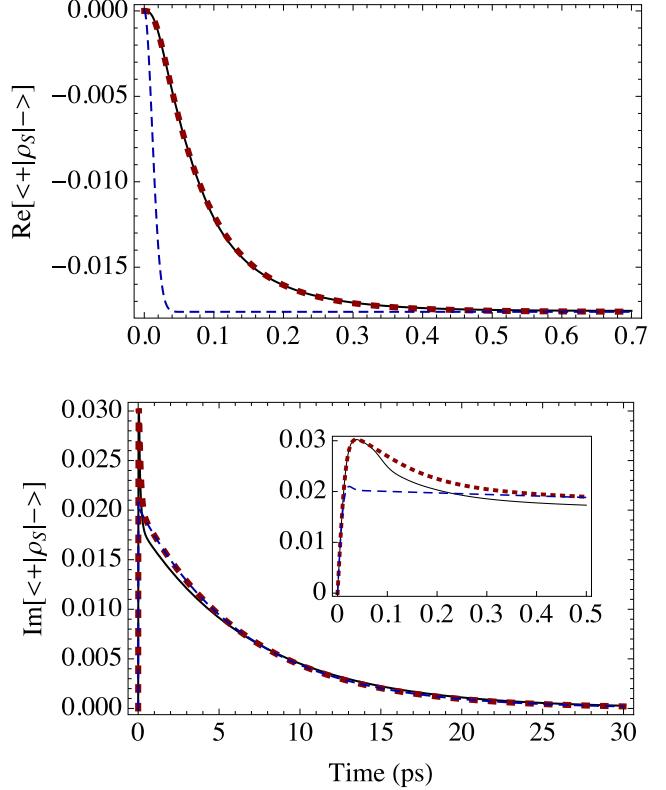


FIG. 3. Dynamics of the coherence for the spin-boson model at ultrastrong coupling: formula (62) (blue dashed line), formula (68) with nonequilibrium short-term corrections (thick red dashed line) in comparison with HEOM (solid black line).

then, due to Eqs. (34) and (36),

$$\begin{aligned} p_m^{(\text{st})} \text{Re} \int_0^\infty \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau \\ = p_n^{(\text{st})} \text{Re} \int_0^\infty \zeta_{mn}(\tau) e^{i(\bar{\varepsilon}_n - \bar{\varepsilon}_m)\tau} d\tau. \end{aligned}$$

Hence, $\text{Im} \rho_{nm}^{(\text{st})} = 0$ and

$$\begin{aligned} \rho_{nm}^{(\text{st})} &= J_{nm} p_n^{(\text{st})} \text{Im} \int_0^\infty \zeta_{mn}(\tau) e^{i(\bar{\varepsilon}_n - \bar{\varepsilon}_m)\tau} d\tau \\ &\quad + J_{nm} p_m^{(\text{st})} \text{Im} \int_0^\infty \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} d\tau. \end{aligned} \quad (64)$$

Consider again our example from Sec. III F. For the same parameters and the same initial state (59), we have calculated the coherence $\langle +|\rho_S(t)|-\rangle$ using formula (62) and compared it with the numerically exact result by HEOM, see Fig. 3. We see that formula (62) correctly predicts the dynamics of the coherence on large times and, in particular, the steady-state coherence.

It is useful to rewrite Eq. (63) also as

$$\rho_{nm}^{(\text{st})} = -J_{nm} p_m^{(\text{st})} \int_0^\beta \zeta_{nm}(-i\beta') e^{(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\beta'} d\beta'. \quad (65)$$

To show the equivalence of this formula to Eq. (63), we can substitute the integral over β' here by the sum of integrals over the segments $[0, i\infty]$, $[i\infty, i\infty + \beta]$, and $[i\infty + \beta, \beta]$. The

first integral is exactly the second term in Eq. (63), the second integral vanishes [since $g_{\alpha\beta}(t)$ indefinitely increases as $t \rightarrow \infty$, which is true in the case of the full decoherence under the unperturbed dynamics—see Eq. (78) below and the end of Sec. III E], and the third integral is equal to the first term in Eq. (63) in view of $p_n^{(\text{st})} = p_m^{(\text{st})} e^{\beta(\bar{\varepsilon}_m - \bar{\varepsilon}_n)}$ [see Eq. (36)] and $\zeta_{nm}(\tau - i\beta) = \zeta_{mn}^*(\tau)$ [see Eqs. (41) and (35)]. From Eq. (65) it is clearly seen that the coherences disappear in the high-temperature limit, which corresponds to the physical intuition. The high-temperature approximation based on formula (65) is developed in Ref. [60].

Remark 6. Previously, we have shown that, in the ultrastrong-coupling limit, the steady state coincides with the mean-force Gibbs state. One can ask if the same is true for the obtained corrections to this limit: Does the steady state calculated in the first-order perturbation theory (with respect to J_{nm}) coincide with the corresponding expression for the mean-force Gibbs state? The corresponding corrections for the mean-force Gibbs state have been derived in Ref. [60]. Formula (65) was first obtained in Ref. [60] as a correction to the mean-force Gibbs state. Here we have derived the same formula as a correction to the steady state to which the dynamics converges. So, the comparison of the results of the present work with those of Refs. [28,60] shows the coincidence of the steady state with the mean-force Gibbs state in the principal order for both populations (the ultrastrong-coupling limit itself) and coherences (the first correction to it) in the pointer basis. It is worthwhile to stress that our results not only prove the fact of convergence but also give the rates of convergence. However, it also should be recalled that here we prove the convergence under assumptions on the spectral density that ensure the full decoherence under the unperturbed dynamics, while the perturbation theory for the mean-force Gibbs state developed in Refs. [28,60] is free of such assumptions.

The dynamical convergence of the system state to the mean-force Gibbs state was also proved (also with the rates of convergence) for weak enough system-bath couplings [51,52,61] (see also Ref. [44] for a more popular explanation of the mathematical results from the cited papers). The mean-force Gibbs state in the high-temperature approximation was obtained in Refs. [62,63]. To obtain mean-force Gibbs states in the case of intermediate coupling and low temperature (i.e., where not one of the mentioned approximations can be used), one can use the reaction coordinate method (see Ref. [64] for some results in this direction) and the so-called “time-evolving matrix product operator” (TEMPO) numerical method [65].

Let us return to Fig. 3. At initial short times, formula (62) gives a significant error because the assumption $\rho(0) = \mathcal{P}\rho(0)$ is not satisfied for state (59). We call a state ρ equilibrium if $\rho = \mathcal{P}\rho$: the bath state is in the equilibrium, which depends on the system state $|n\rangle$. In this sense, state (59) is nonequilibrium. In the next section, we derive the nonequilibrium corrections for initial short times.

B. Nonequilibrium corrections

Consider now the initial system-bath state of the form

$$\rho(0) = \sum_n p_n(0) |n\rangle \langle n| \otimes \rho_B. \quad (66)$$

Thus, now

$$\mathcal{Q}\rho(0) = \sum_n p_n(0) |n\rangle \langle n| \otimes (\rho_B - \rho_B^{(n)}). \quad (67)$$

The substitution of the expression (A8) for $\mathcal{Q}\rho(t)$ into Eq. (61) gives

$$\rho_{nm}(t) = \rho_{nm}^{(\text{eq})}(t) + \rho_{nm}^{(\text{noneq})}(t), \quad (68)$$

where $\rho_{nm}^{(\text{eq})}(t)$ is given by Eq. (62) and

$$\begin{aligned} \rho_{nm}^{(\text{noneq})}(t) &= iJ_{nm} \int_0^t d\tau e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \\ &\times \{p_n(0)[\zeta_{mn}^*(t, \tau) - e^{-i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \zeta_{mn}^*(\tau)] \\ &- p_m(0)[\zeta_{mm}(t, \tau) - e^{-i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \zeta_{nm}(\tau)]\}. \end{aligned} \quad (69)$$

Here,

$$\begin{aligned} \zeta_{mn}(t, \tau) &= \left\langle \exp \left\{ i \left(H_B + \sum_\alpha \theta_{\alpha m} B_\alpha \right) t \right\} \right. \\ &\times \exp \left\{ -i \left(H_B + \sum_\alpha \theta_{\alpha n} B_\alpha \right) \tau \right\} \\ &\left. \times \exp \left\{ -i \left(H_B + \sum_\alpha \theta_{\alpha l} B_\alpha \right) (t - \tau) \right\} \right\rangle. \end{aligned}$$

In Appendix B, we show that

$$\begin{aligned} \zeta_{mn}(t, \tau) &= \exp \left\{ - \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta l}) g_{\alpha\beta}(\tau) \right. \\ &+ \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m}) [\theta_{\beta m} g_{\alpha\beta}^*(t) - \theta_{\beta l} g_{\alpha\beta}(t)] \\ &+ \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha l}) [\theta_{\beta l} g_{\alpha\beta}(t - \tau) \\ &\left. - \theta_{\beta m} g_{\alpha\beta}^*(t - \tau)] \right\}. \end{aligned} \quad (70)$$

Note that analogous traces for fermionic baths were calculated in Ref. [47]. Thus,

$$\begin{aligned} \zeta_{mm}(t, \tau) &= \exp \left\{ - \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) g_{\alpha\beta}(\tau) \right. \\ &- 2i \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m}) \theta_{\beta m} \text{Im}[g_{\alpha\beta}(t) \\ &\left. - g_{\alpha\beta}(t - \tau)] \right\}. \end{aligned} \quad (71)$$

Let us show that

$$\lim_{t \rightarrow \infty} \zeta_{mm}(t, \tau) = e^{-i(\bar{\varepsilon}_m - \bar{\varepsilon}_n)\tau} \zeta_{mm}(\tau), \quad (72)$$

and, thus, nonequilibrium correction (69) vanishes for long times. Since both $\zeta_{mm}(t, \tau)$ and $\zeta_{mm}(\tau)$ vanish for large τ , it is sufficient to prove that

$$-2 \lim_{t \rightarrow \infty} \text{Im}[g_{\alpha\beta}(t) - g_{\alpha\beta}(t - \tau)] = (\delta\varepsilon_{\alpha\beta} + \delta\varepsilon_{\beta\alpha})\tau \quad (73)$$

for an arbitrary constant τ . From Eqs. (45b) and (49), we have

$$\begin{aligned} -2 \operatorname{Im} g_{\alpha\beta}(t) &= i[g_{\alpha\beta}(t) - g_{\beta\alpha}(-t)] \\ &= -i \int_0^\infty d\omega \left\{ \frac{\mathcal{J}_{\alpha\beta}(\omega)}{\omega^2} (e^{-i\omega t} + i\omega t - 1) \right. \\ &\quad \left. - \frac{\mathcal{J}_{\beta\alpha}(\omega)}{\omega^2} (e^{i\omega t} - i\omega t - 1) \right\} \end{aligned} \quad (74)$$

and

$$\begin{aligned} -2 \operatorname{Im} [g_{\alpha\beta}(t) - g_{\alpha\beta}(t - \tau)] &= \tau \int_0^\infty d\omega \frac{\mathcal{J}_{\alpha\beta}(\omega) + \mathcal{J}_{\beta\alpha}(\omega)}{\omega} \\ &\quad + \int_0^\infty d\omega \left\{ \frac{\mathcal{J}_{\alpha\beta}(\omega)}{\omega^2} e^{-i\omega t} (1 - e^{i\omega\tau}) \right. \\ &\quad \left. - \frac{\mathcal{J}_{\beta\alpha}(\omega)}{\omega^2} e^{i\omega t} (1 - e^{-i\omega\tau}) \right\}. \end{aligned} \quad (75)$$

Here, the first integral is exactly the right-hand side of Eq. (73), whereas the second integral disappears either for large t due to the Riemann-Lebesgue theorem (if τ is such that $e^{\pm i\omega\tau} \neq 1$) or for all t (if $e^{\pm i\omega\tau} = 1$). This proves limits (73) and (72). For the Drude-Lorentz spectral density, from Eq. (58), we see that the convergence is exponential with the rate Ω .

In Fig. 3, we see a very good agreement of formula (68) with the numerically exact results.

C. Rate of decoherence and range of validity of the approximation

Now let us consider the initial system-bath state of the form

$$\rho(0) = \rho_S(0) \otimes \rho_B, \quad (76)$$

where $\rho_S(0)$ is an arbitrary (not necessarily diagonal anymore) initial-system state. Substitution of Eq. (A8) into Eq. (61) gives

$$\rho_{nm}(t) = \rho_{nm}^{(\text{decoh})} + \rho_{nm}^{(\text{eq})}(t) + \rho_{nm}^{(\text{noneq})}(t) + \rho_{nm}^{(\text{coh-coh})}(t), \quad (77)$$

where

$$\begin{aligned} \rho_{nm}^{(\text{decoh})}(t) &= \rho_{nm}(0) \zeta_{mnn}(t, 0) e^{i(\varepsilon_m - \varepsilon_n)t} \\ &= \rho_{nm}(0) e^{i(\varepsilon_m - \varepsilon_n)t} \\ &\quad \times \exp \left\{ - \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m}) [\theta_{\beta n} g_{\alpha\beta}(t) \right. \\ &\quad \left. - \theta_{\beta m} g_{\alpha\beta}^*(t)] \right\} \end{aligned} \quad (78)$$

describes the decoherence in the basis $\{|n\rangle\}$ [note that $\zeta_{mnn}(t, \tau)$ is independent of τ] and

$$\begin{aligned} \rho_{nm}^{(\text{coh-coh})}(t) &= i \sum_{l \neq n, m} \int_0^t d\tau \{ \rho_{nl}(0) J_{lm} \zeta_{nml}^*(t, \tau) e^{i[\varepsilon_m \tau - \varepsilon_n t + \varepsilon_l(t - \tau)]} \\ &\quad - \rho_{lm}(0) J_{nl} \zeta_{mnl}(t, \tau) e^{i[\varepsilon_m t - \varepsilon_n \tau - \varepsilon_l(t - \tau)]} \} \end{aligned} \quad (79)$$

describes the coherence-coherence transfer.

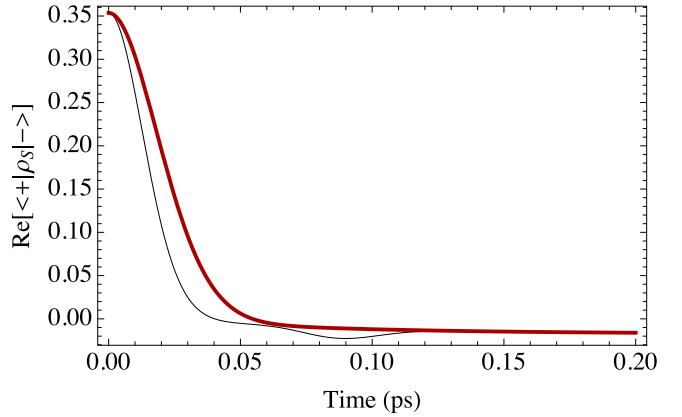


FIG. 4. Decoherence for the spin-boson model at ultrastrong coupling: formula (77) (thick red line) in comparison with the numerically exact method of HEOM (thin black line) for the initial state (80).

Note also that $\mathcal{Q}\rho(0) \neq 0$ gives contributions also to the initial dynamics of $\mathcal{P}\rho(t)$ (i.e., populations in our case), see Eq. (A9) and Refs. [37,43]. However, here, we neglect this influence.

In this section, we focus on the decoherence term. Let us consider the initial state

$$\rho(0) = \left(\cos \frac{\pi}{8} |1\rangle + \sin \frac{\pi}{8} |0\rangle \right) \left(\cos \frac{\pi}{8} \langle 1| + \sin \frac{\pi}{8} \langle 0| \right) \otimes \rho_B \quad (80)$$

for our example. From one side, it has initial coherences in the pointer basis $\{|+\rangle, |-\rangle\}$. From the other side, the populations in this basis are not stationary. The other parameters are the same.

In Fig. 4, we again compare our approximation [formula (77)] and the numerically exact solution and find a good precision of formula (77) for our case. Our approximation slightly underestimates the rate of decoherence. One might guess that the cause is that formula (78) takes into account the pure decoherence only due to the dynamics of differently displaced baths and does not take into account the decoherence due to the transitions in the basis $\{|+\rangle, |-\rangle\}$. However, a simulation (not shown here) shows that taking into account the decoherence due to depopulation according to the simple well-known 1/2 rule (adding the decoherence rate equal to one half of the sum of the depopulation rates of the involved states) has only a negligible effect. The reason is that the relaxation of populations occurs on much larger timescales, which we discuss below. Correspondingly, the depopulation rates are much smaller than the pure decoherence rate.

In Fig. 5, we show the trace distance of $\rho_S(t)$ to the diagonal part of $\rho_S(0)$, i.e., to $\rho_S^{(\text{diag})}(0)$, where

$$\begin{aligned} \rho_S^{(\text{diag})}(t) &= |+\rangle \langle +| \rho_S(t) |+\rangle \langle +| \\ &\quad + |-\rangle \langle -| \rho_S(t) |-\rangle \langle -. \end{aligned} \quad (81)$$

We clearly see two timescales: rapid decoherence to a state close to the projection $\mathcal{P}\rho(0)$ and further slow evolution toward the steady state. The same timescale separation in the ultrastrong-coupling regime was numerically observed in Ref. [31].

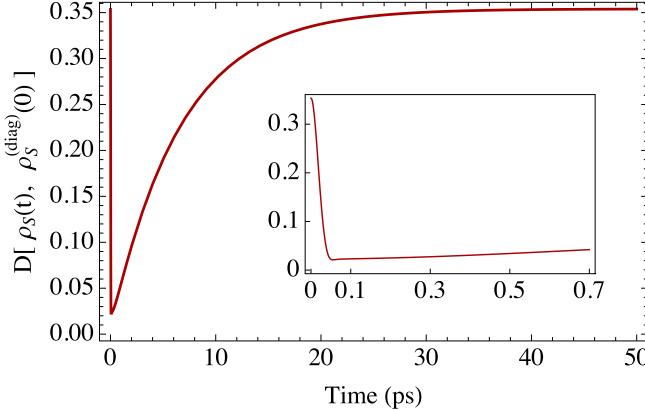


FIG. 5. For the example in Fig. 4, the trace distance of $\rho_S(t)$ to the diagonal part $\rho_S^{(\text{diag})}(0)$ of the initial system state $\rho_S(0)$, Eq. (81).

This may resolve a discussion in the papers [27,28] about the correct form of the steady state at ultrastrong coupling. Namely, the projection $\mathcal{P}\rho(0)$ is quasisteady and becomes an exact steady state in the quantum Zeno limit ($\theta_{\alpha n} \rightarrow \infty$ for all α and n), or, in other words, in the limit of not even ultrastrong but infinitely strong-coupling limit. However, in the case of finitely large interaction, it is quasisteady and the mean-force Gibbs state is the only true steady state. The rate of convergence to the mean-force Gibbs state decreases to zero when the system-bath interaction strength indefinitely increases.

For comparison, Fig. 6 shows the trace distance of $\rho_S(t)$ to the time-dependent diagonal part $\rho_S^{(\text{diag})}(t)$. It is another illustration of the rapid relaxation toward the subspace \mathcal{PS} (see the beginning of Sec. III B) and the further slow evolution in the neighborhood of this subspace.

Now we can discuss the range of validity of the presented approach. The approach is essentially based on the described time separation: Evolution in the neighborhood of the subspace \mathcal{PS} should be much slower than the relaxation toward this subspace. As we described in Sec. III B, relaxation toward this subspace has two parts: the decoherence and the displaced bath relaxation.

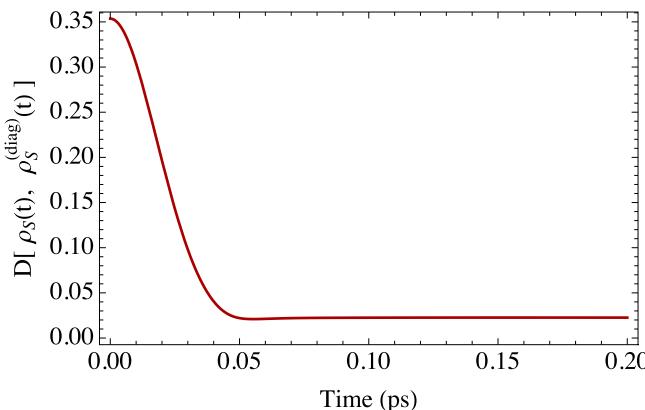


FIG. 6. For the example in Fig. 4, the trace distance of $\rho_S(t)$ to the time-dependent diagonal part $\rho_S^{(\text{diag})}(t)$, Eq. (81).

The rate of the displaced bath relaxation can be associated with the rate of convergence of limit (72). In the case of the Drude-Lorentz spectral density (54), it is equal to Ω .

The rates of decoherence are given by the quantities

$$\sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) \text{Re}[g_{\alpha\beta}(t)], \quad (82)$$

from Eq. (78). The same quantity enters ζ_{nm} , which, according to Eq. (62), defines the magnitude of coherences. The magnitude of coherences should be small for the validity of the approach. For $t \gg \Omega^{-1}$, expression (82) is approximately equal to $r_{nm}^{(\text{decoh})} t$, where

$$r_{nm}^{(\text{decoh})} = \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) \frac{2\eta}{\beta\Omega}. \quad (83)$$

Thus, the transition rates γ_{nm} describing the evolution in the neighborhood of \mathcal{PS} should be smaller than both Ω and Eq. (83). This condition is satisfied either for small J_{nm} or for large system-bath couplings $\eta\theta_{\alpha n}$ (i.e., for an ultrastrong coupling) or small β (i.e., for a large temperature).

It is interesting to note that, if the temperature is large, then the described approximation holds even for moderate (not ultrastrong) system-bath couplings. So, the described strong-decoherence approximation is more general than the ultrastrong-coupling approximation. This observation is consistent with numerical results of Ref. [63], which show that the high-temperature approximation for the mean-force Gibbs state works in the case of either high temperature or strong coupling (and a moderate temperature).

Also, we see that, for all $n \neq m$, the difference $|\theta_{\alpha n} - \theta_{\alpha m}|$ should not be small, at least for some α . We assumed that the nonzero $\theta_{\alpha n}$ are not degenerate. So, we should assume also that they are even not quasidegenerate. The case of degenerate and quasidegenerate $\theta_{\alpha n}$ is analyzed in the next section.

V. STRONG-DECOHERENCE APPROXIMATION: GENERAL CASE

A. Decomposition of the Hamiltonian

In this section we describe the strong-decoherence approximation in the general case. First, we release assumptions (i) and (ii) in Sec. III A. Namely, we allow for the case

$$A_\alpha = \sum_n \theta_{\alpha n} \Pi_n, \quad (84)$$

where Π_n are orthogonal projectors such that $\sum_n \Pi_n = I_S$ (the identity operator in \mathcal{H}_S), but not necessarily one-dimensional projectors. Without loss of generality, we assume that, for each α , all $\theta_{\alpha n}$ are different.

Second, we allow for small corrections to Eq. (84). For example, in the end of the previous section, a possibility of quasidegeneracies in $\theta_{\alpha n}$ is mentioned. They can be expressed as sums of exactly degenerate $\theta_{\alpha n}$ and small corrections. Moreover, we allow for small corrections of a more general form, not necessarily of the decoherence type. Namely, we decompose of the interaction Hamiltonian in the following

way:

$$\begin{aligned} H_I &= \sum_{\alpha=1}^M A_\alpha \otimes B_\alpha \\ &= \sum_n \sum_{\alpha=1}^M \theta_{\alpha n} \Pi_n \otimes B_\alpha + \sum_{\alpha=1}^M \delta A_\alpha \otimes B_\alpha, \end{aligned}$$

where

$$\delta A_\alpha = A_\alpha - \sum_n \theta_{\alpha n} \Pi_n. \quad (85)$$

Since

$$\delta A_\alpha = \sum_n \Pi_n \delta A_\alpha \Pi_n + \sum_{n \neq m} \Pi_n A_\alpha \Pi_m,$$

we can write

$$H_I = \sum_n \sum_{\alpha=1}^M \theta_{\alpha n} \Pi_n \otimes B_\alpha \quad (86a)$$

$$+ \sum_{n \neq m} \sum_{\alpha=1}^M \Pi_n A_\alpha \Pi_m \otimes B_\alpha \quad (86b)$$

$$+ \sum_n \sum_{\alpha=1}^M \Pi_n \delta A_\alpha \Pi_n \otimes B_\alpha^{(n)} \quad (86c)$$

$$- \sum_n \sum_{\alpha=1}^M (\delta \varepsilon_{\alpha n} + \delta \varepsilon_{n \alpha}) \Pi_n \delta A_\alpha \Pi_n, \quad (86d)$$

where we have introduced the displaced operators

$$\begin{aligned} B_\alpha^{(n)} &= \int [\overline{d_\alpha(\xi)} a_n(\xi) + d_\alpha(\xi) a_n(\xi)^\dagger] d\xi \\ &= B_\alpha + \sum_{\beta=1}^M \theta_{\beta n} (\delta \varepsilon_{\alpha \beta} + \delta \varepsilon_{\beta \alpha}) \end{aligned} \quad (87)$$

such that

$$\text{Tr} \rho_B^{(n)} B_\alpha^{(n)} = 0. \quad (88)$$

Term (86a) describes pure decoherence between the subspaces $\mathcal{H}_S^{(n)} = \Pi_n \mathcal{H}_S$. It is assumed to be large, thus giving the name for the approximation (the strong-decoherence approximation). Term (86d) can be assigned to the system Hamiltonian and, thus, is not required to be small.

Terms (86b) and (86c) are assumed to be small. Term (86b) is responsible for transitions between different subspaces $\mathcal{H}_S^{(n)}$, along with the off-diagonal terms of the system Hamiltonian

$$V = \sum_{n \neq m} \Pi_n H_S \Pi_m. \quad (89)$$

Term (86c) is responsible for the weak-coupling dynamics inside each subspace.

Thus, we have the following decomposition of the Hamiltonian into a reference part H_0 and a small perturbation H' :

$$H = H_0 + H', \quad (90)$$

where

$$\begin{aligned} H_0 &= \sum_n \left\{ \Pi_n H_S \Pi_n - \sum_{\alpha=1}^M (\delta \varepsilon_{\alpha n} + \delta \varepsilon_{n \alpha}) \Pi_n \delta A_\alpha \Pi_n \right\} \\ &\quad + H_B + \sum_n \sum_{\alpha=1}^M \theta_{\alpha n} B_\alpha \end{aligned}$$

and

$$H' = V + \sum_n H_I^{(n)} + \sum_{n \neq m} \Pi_n A_\alpha \Pi_m \otimes B_\alpha, \quad (91)$$

$$H_I^{(n)} = \Pi_n \delta A_\alpha \Pi_n \otimes B_\alpha^{(n)}. \quad (92)$$

We again introduce the Hamiltonian of displaced oscillators $H_B^{(n)}$ (22) so that

$$H_B^{(n)} = H_B + \sum_{\alpha=1}^M \theta_{\alpha n} B_\alpha + \delta \varepsilon_n \quad (93)$$

and express

$$H_0 = \sum_n (\bar{H}_S^{(n)} + H_B^{(n)}), \quad (94)$$

where

$$\begin{aligned} \bar{H}_S^{(n)} &= \Pi_n H_S \Pi_n - \delta \varepsilon_n \Pi_n \\ &\quad - \sum_{\alpha=1}^M (\delta \varepsilon_{\alpha n} + \delta \varepsilon_{n \alpha}) \Pi_n \delta A_\alpha \Pi_n. \end{aligned} \quad (95)$$

B. Projection operator

Again, the unperturbed dynamics governed by H_0 leads to fast decoherence with respect to the subspaces $\mathcal{H}_S^{(n)}$, hence, the density operator quickly becomes block diagonal: $\rho = \sum_n \rho^{(n)}$, where $\rho^{(n)} \in \mathcal{S}^{(n)} = \Pi_n \mathcal{S} \Pi_n$. Also, again from Eqs. (94) and (95), we see that the fast dynamics in the subspaces $\mathcal{S}^{(n)}$ as well as that the dynamics of the system and the bath inside each subspace are decoupled from each other. Since, inside each subspace, the bath quickly thermalizes, we can define the projection operator as Eq. (26), where Π_n is now, in general, multidimensional.

The slow dynamics consists of the dynamics inside each subspace according to the weak-coupling theory and transitions between different subspaces. The weak-coupling dynamics inside each subspace is defined by the Hamiltonian

$$H^{(n)} = \bar{H}_S^{(n)} + H_B^{(n)} + H_I^{(n)} \quad (96)$$

and the bath equilibrium state $\rho_B^{(n)}$. The transitions between different subspaces are governed by the off-diagonal blocks of H' . Fast and slow dynamics can be again schematically represented by Fig. 1 with a slightly modified bottom part for $\rho^{(n)} = \Pi_n \rho(t) \Pi_n$ given in Fig. 7.

Note that master equations based on projection operators onto multidimensional subspaces were previously derived in spin chemistry [66]. This can be seen as a particular case of the presented approach. Other known particular cases are presented in the next section.

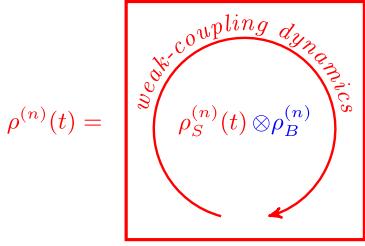


FIG. 7. Modification of the bottom part of Fig. 1 for the general strong-decoherence coupling. Now Π_n are projectors onto, in general, multidimensional system subspaces. The dimensions are not necessarily equal. The blue color denotes the fast processes and degrees of freedom and the red color denotes the slow ones. The slow processes are described by a quantum master equation. Here, $\rho^{(n)}(t) = \Pi_n \rho(t) \Pi_n$ and $\rho_S^{(n)}(t) = \Pi_n \rho_S(t) \Pi_n$. The weak-coupling dynamics consists of the fast bath relaxation toward the (displaced) equilibrium state $\rho_B^{(n)}$ and the slow dynamics of $\rho_S^{(n)}(t)$.

C. Particular cases

1. Generalized Förster theory

In Sec. III, we introduced a simple (nondegenerate) version of the strong-decoherence approximation as a generalization of the Förster approximation. The presented version with multidimensional projectors Π_n includes the generalized Förster theory [67]. In biological light-harvesting complexes one often faces with the case of weakly coupled clusters of molecules. But the dipole couplings between the molecules inside each cluster are not small. The generalized Förster theory describes transitions between the cluster. The dynamics inside each cluster can be described in various approximations [68], including the Redfield (weak-coupling) approximation [69], which is our case.

Note that, in Ref. [70], another projection operator is proposed for the generalized Förster theory:

$$\mathcal{P}\rho = \sum_n p_n Z_n^{-1} e^{-\beta H^{(n)}}, \quad (97)$$

where $Z_n = \text{Tr}e^{-\beta H^{(n)}}$ and $p_n = \text{Tr}\Pi_n\rho$. This means that the system-bath coupling inside each cluster is not weak and the system and the bath thermalize together to their “global” thermal state, i.e., with respect to $H^{(n)}$. This thermalization process is treated as “fast.” In our approximation, the system-bath coupling inside each cluster is weak, so, the bath alone thermalizes much faster than the system, which leads to projection operator (26).

2. Modified Redfield theory

Consider again the EET Hamiltonian H_S (13), where $|n\rangle$ corresponds to an excitation on molecule n , and $A_\alpha \equiv A_n = |n\rangle\langle n|$. Let the spectrum H_S be nondegenerate and the intersite couplings J_{nm} be small compared with the local excitation energies ε_n . Then the eigenvectors $|e_n\rangle$ of H_S are highly localized: $\langle e_n|m\rangle$ are small if $n \neq m$. Put $\Pi_n = |e_n\rangle\langle e_n|$. Then $V = 0$ and [see Eq. (91)]

$$H' = \sum_k \sum_{n \neq m} \langle e_n|k\rangle \langle k|e_m\rangle |e_n\rangle\langle e_m| \otimes B_\alpha \quad (98)$$

is the off-diagonal of the interaction Hamiltonian in the eigenbasis of the system Hamiltonian. For each k , at least one of the scalar products $\langle e_n|k\rangle$ and $\langle k|e_m\rangle$ is small. Hence, H' can be treated as a small perturbation even if the system-bath coupling is large. In the theory of EET, this approximation is referred to as the modified Redfield approximation, in contrast to the usual (“standard”) Redfield approximation (or the weak-coupling approximation), where the whole interaction Hamiltonian is treated perturbatively.

So, the range of validity of the modified Redfield approach intersects with that of the Förster approach. The difference is that the Förster approach considers the decoherence in the local basis as the primary process, while the modified Redfield—the decoherence is in the eigenbasis.

From another side, the usual weak-coupling approach also falls into the modified Redfield approach whenever all energy levels are nondegenerate and well separated from each other. This ensures the fast decoherence despite of the fact that the diagonal part of H_I is also weak.

The modified Redfield theory fails if there are some degenerate or nearly degenerate energy levels [36,41,42]. This was considered as a technical limitation which can be overcome by the inclusion of nonsecular terms (pumping of coherences from the populations). However, in Ref. [43], where such terms were introduced, it is argued that this limitation is fundamental since the basic assumption of strong decoherence between different eigenvectors is not satisfied.

Hence, a hybrid consideration where the dynamics inside the subspaces of degenerate or nearly degenerate levels is described in the weak-coupling approximation, while the transitions between these subspaces is treated by using the modified Redfield approach, can be useful. This falls into the proposed general formalism.

Combinations of the modified Redfield and the Förster approaches are also widely used in the theory of EET [36,42,71,72] and also can be considered within the proposed formalism.

D. Master equation

Substitution of interaction Hamiltonian (91) and projection operator (26) to the general Markovian master equation (29) gives

$$\dot{\rho}_S^{(d)}(t) = \sum_n \mathcal{R}_n \rho_S^{(d)}(t) + \sum_{m \neq n} \mathcal{T}_{nm} \rho_S^{(d)}(t), \quad (99)$$

where

$$\rho_S^{(d)} = \text{Tr}_B \mathcal{P}\rho = \sum_n \Pi_n \rho_S \Pi_n \equiv \sum_n \rho_S^{(n)}, \quad (100)$$

$$\mathcal{R}_n(t) \rho_S^{(d)} = \int_0^\infty d\tau \text{Tr}_B \{ \mathcal{L}'_n(t) \mathcal{L}'_n(t-\tau) [\rho_S^{(n)} \otimes \rho_B^{(n)}] \} \quad (101)$$

is the Redfield generator in the subspace $\mathcal{H}_S^{(n)}$ with $\mathcal{L}'_n(t) = [H_I^{(n)}, \cdot]$, while \mathcal{T}_{nm} come from the off-diagonal contributions to H' and describe the transitions between different subspaces. Namely, for fixed n and m , \mathcal{T}_{nm} describes transitions from the subspace $\mathcal{H}_S^{(m)}$ to the subspace $\mathcal{H}_S^{(n)}$.

For completeness, let us give an explicit expression for the Redfield generator:

$$\begin{aligned} \mathcal{R}_n \rho_S^{(d)} = & -i[H_{LS}^{(n)}, \rho_S^{(d)}] + \sum_{\alpha, \beta=1}^M \sum_{\omega, \omega' \in \mathcal{F}_n} e^{i(\omega' - \omega)t} \\ & \times \gamma_{\alpha\beta}(\omega, \omega') \left(A_{\beta n \omega} \rho_S^{(d)} A_{\alpha n \omega'}^\dagger \right. \\ & \left. - \frac{1}{2} \{ A_{\alpha n \omega'}^\dagger A_{\beta n \omega}, \rho_S^{(d)} \} \right), \end{aligned} \quad (102)$$

where

$$H_{LS}^{(n)} = \sum_{\alpha, \beta=1}^M \sum_{\omega, \omega' \in \mathcal{F}_n} e^{i(\omega' - \omega)t} S_{\alpha\beta}(\omega, \omega') A_{\alpha n \omega'}^\dagger A_{\beta n \omega} \quad (103)$$

(the subindex LS stands for the Lamb shift). Here \mathcal{F}_n is the spectrum of $[\bar{H}_S^{(n)}, \cdot]$, or, in other words, the set of all Bohr frequencies (all differences between eigenvalues) of $\bar{H}_S^{(n)}$. Note that \mathcal{F}_n includes positive and negative Bohr frequencies and the zero Bohr frequency. Denote $\text{spec}\bar{H}_S^{(n)}$ the spectrum of $\bar{H}_S^{(n)}$ and P_ε the projector onto the eigenspace corresponding to $\varepsilon \in \text{spec}\bar{H}_S^{(n)}$. Put $P_\varepsilon \equiv 0$ whenever $\varepsilon \notin \text{spec}\bar{H}_S^{(n)}$. Then, $A_{\alpha n} = \Pi_n \delta A_\alpha \Pi_n$,

$$A_{\alpha n \omega} = \sum_{\varepsilon \in \text{spec}\bar{H}_S^{(n)}} P_{\varepsilon - \omega} A_{\alpha n} P_\varepsilon, \quad (104)$$

so that $[\bar{H}_S^{(n)}, A_{\alpha n \omega}] = -\omega A_{\alpha n \omega}$. Also,

$$\begin{aligned} \gamma_{\alpha\beta}(\omega, \omega') &= \Gamma_{\alpha\beta}(\omega) + \Gamma_{\beta\alpha}^*(\omega'), \\ S_{\alpha\beta}(\omega, \omega') &= \frac{1}{2i} [\Gamma_{\alpha\beta}(\omega) - \Gamma_{\beta\alpha}^*(\omega')], \\ \Gamma_{\alpha\beta}(\omega) &= \int_0^\infty d\tau e^{i\omega\tau} \langle e^{iH_B\tau} B_\alpha e^{-iH_B\tau} B_\beta \rangle. \end{aligned} \quad (105)$$

The intersubspace transition superoperators \mathcal{T}_{nm} are derived completely analogously:

$$\begin{aligned} \mathcal{T}_{nm} \rho_S^{(d)} = & -i[H_{LS}^{(nm)}, \rho_S^{(d)}] \\ & + \sum_{\alpha, \beta=0}^M \sum_{\omega, \omega' \in \mathcal{F}_{nm}} e^{i(\omega' - \omega)t} \gamma_{\alpha\beta nm}(\omega, \omega') \\ & \times \left(A_{\beta nm \omega} \rho_S^{(d)} A_{\alpha nm \omega'}^\dagger - \frac{1}{2} \{ A_{\alpha nm \omega'}^\dagger A_{\beta nm \omega}, \rho_S^{(d)} \} \right), \end{aligned} \quad (106)$$

where

$$H_{LS}^{(nm)} = \sum_{\alpha, \beta=0}^M \sum_{\omega, \omega' \in \mathcal{F}_{nm}} e^{i(\omega' - \omega)t} S_{\alpha\beta nm}(\omega, \omega') A_{\alpha nm \omega'}^\dagger A_{\beta nm \omega}. \quad (107)$$

Here, we have formally put $A_0 \equiv V$ and $B_0 \equiv I_B$ (the identity operator in the bath Hilbert space). Furthermore, \mathcal{F}_{nm} is the set of differences $\varepsilon' - \varepsilon$, where $\varepsilon' \in \text{spec}\bar{H}_S^{(m)}$ and $\varepsilon \in \text{spec}\bar{H}_S^{(n)}$. So, the union of all \mathcal{F}_n and all \mathcal{F}_{nm} is the set of the Bohr frequencies of the diagonal part of the system Hamiltonian

$$\bar{H}_S^{(d)} = \sum_n \bar{H}_S^{(n)}. \quad (108)$$

Then, $A_{\alpha nm} = \Pi_n A_\alpha \Pi_m$ and

$$A_{\alpha nm \omega} = \sum_{\varepsilon \in \text{spec}\bar{H}_S^{(m)}} P_{\varepsilon - \omega} A_{\alpha nm} P_\varepsilon, \quad (109)$$

so that $[\bar{H}_S^{(d)}, A_{\alpha nm \omega}] = -\omega A_{\alpha nm \omega}$. Also,

$$\gamma_{\alpha\beta nm}(\omega, \omega') = \Gamma_{\alpha\beta nm}(\omega) + \Gamma_{\beta\alpha nm}^*(\omega'), \quad (110)$$

$$\begin{aligned} S_{\alpha\beta nm}(\omega, \omega') &= \frac{1}{2i} [\Gamma_{\alpha\beta nm}(\omega) - \Gamma_{\beta\alpha nm}^*(\omega')], \\ \Gamma_{\alpha\beta nm}(\omega) &= \int_0^\infty d\tau e^{i\omega\tau} \langle e^{iH_B^{(m)}\tau} B_\alpha e^{-iH_B^{(n)}\tau} B_\beta \rangle_m \\ &\equiv \int_0^\infty d\tau e^{i\omega\tau} \zeta_{\alpha\beta nm}(\tau). \end{aligned} \quad (111)$$

Note that the previously defined functions $\zeta_{nm}(\tau)$ [see Eq. (41)] coincide with $\zeta_{00nm}(\tau)$.

Although the generator looks like the Franke-Gorini-Kossakowski-Lindblad-Sudarshan (FGKLS) form,¹ it is not of the FGKLS form because the matrices $\gamma_{\alpha\beta}(\omega, \omega')$ and $\gamma_{\alpha\beta nm}(\omega, \omega')$ [with two double indexes $i = (\alpha, \omega')$ and $j = (\beta, \omega)$] are, in general, not positive-semidefinite. However, if all exponents $e^{i(\omega' - \omega)t}$ for $\omega' \neq \omega$ can be treated as rapidly oscillating, then we can drop all the terms with $\omega' \neq \omega$ (secular approximation). Then, for each ω , the matrices $\gamma_{\alpha\beta}(\omega, \omega)$ and $\gamma_{\alpha\beta nm}(\omega, \omega)$ (with the simple indices α and β) are positive-semidefinite. Hence, the master equation becomes of the first standard FGKLS form [26].

If the secular approximation cannot be applied, then another approximation [namely, a partial secular approximation and small modifications in the arguments of rate constants $\gamma_{\alpha\beta}(\omega)$ and $\gamma_{\alpha\beta nm}(\omega)$] can be applied to obtain a master equation in the FGKLS form [78].

Usually, the fact that the Redfield equation is not of the FGKLS form and does not conserve positivity is treated as a shortcoming of this equation (though compensated by a higher precision). However, in Ref. [79], it is argued that nonpositivity of the Redfield equation is natural and caused by the fact that this equation is more suitable to describe the dynamics of initially correlated system and bath. In this case, the dynamical map does not need to be completely positive. The same kind of arguments can be applied for the derived non-FGKLS generator.

Remark 7. The dynamical map $\rho_S(0) \mapsto \rho_S(t)$ defined by

$$\rho_S(t) = \text{Tr}_B \{ e^{-iH_t} [\rho_S(0) \otimes \rho_B(0)] e^{iH_t} \} \equiv \Lambda_t [\rho_S(0)], \quad (112)$$

where $\rho_B(0)$ is an arbitrary fixed initial state of the bath, is well known to be completely positive. Consider now a more general dynamical map of the form

$$\rho_S(t) = \text{Tr}_B \{ e^{-iH_t} \mathcal{A}[\rho_S(0)] e^{iH_t} \}, \quad (113)$$

where \mathcal{A} is a linear assignment map, which assigns a system-bath state to an arbitrary reduced state of the system $\rho_S(0)$

¹The abbreviations GKLS or GKSL are more common [73–75]; however, in the same 1976, this general form of a generator of a quantum dynamical semigroup was also proposed by Franke [76], see also Ref. [77].

from a certain domain. Its physical meaning is a preparation of a correlated system-bath state with the reduced state of the system $\rho_S(0)$ [i.e., $\text{Tr}_B \mathcal{A}[\rho_S(0)] = \rho_S(0)$]. For example, a correlated state may be a result of the past interaction of the system and the bath.

However, in general, not an arbitrary reduced state of the system can arise as an outcome of this preparation process. If we somehow prepare an arbitrary state of the system and simply attach it to the environment (so that their initial state is a product state), then, by construction, any initial state of the system can be considered. But if the system and the environment interacted in the past and have produced a correlated state (which we treat as the “initial” one), then, in general, not an arbitrary reduced state of the system could arise in such process. Even if we started from an arbitrary system state in the past, the interaction with the bath changes this state. This means that the map \mathcal{A} is physically meaningful only on a subset of the density operators of the system: for those which are accessible for the given preparation procedure. There is no physical contradiction if $\mathcal{A}[\rho_S(0)]$ is nonpositive for a $\rho_S(0)$ which is inaccessible for this procedure.

Moreover, there is a mathematical theorem that, under the described conditions, the map \mathcal{A} preserves positivity for all density operators of the system $\rho_S(0)$ if and only if \mathcal{A} is a product map, i.e., $\mathcal{A}[\rho_S(0)] = \rho_S(0) \otimes \rho_B(0)$ for all $\rho_S(0)$ and a fixed $\rho_B(0)$ [80,81]. Otherwise, \mathcal{A} with necessity violates positivity for some density operators of the system. Quantum dynamics beyond complete positivity is actively studied [82–85].

A common view on the cause of violation of positivity in solutions of the Redfield equation is the fast non-Markovian relaxation process of the initial product state to an adjusted (correlated) system-bath state [86]. During this fast relaxation process, the dynamics is not described by the Redfield (or another Markovian) master equation. The Redfield equation describes the dynamics starting with a correlated, adjusted system-bath state. This means that the Redfield equation actually approximates not dynamics (112), but dynamics (113), where the map \mathcal{A} describes the adjusted system-bath states that can arise from this fast initial non-Markovian stage of evolution. In Ref. [79], an expression for this map is derived using the perturbation theory for the weak-coupling limit.

As we said above, \mathcal{A} preserves positivity for the physically accessible reduced states of the system and, generally speaking, violates positivity for the inaccessible states. If the solution of the Cauchy problem for the Redfield equation with an initial state $\rho_S(0)$ is nonpositive, then the state $\mathcal{A}[\rho_S(0)]$ cannot emerge during the first stage of the evolution. If we start with a product state $\rho_S(0) \otimes \rho_B(0)$, then we should approximate the initial stage of evolution by another method (e.g., simply Dyson series or a master equation of the FGKLS form or a cumulant approach [87–92]) and only then switch to the Redfield equation [93,94]. The same is true for the derived more general “Redfield-like” equation (99).

Resuming, the reduced density operator of the system $\rho_S(t)$ must be positive for all times. However, the Redfield equation or the analogous derived equation (99) may violate positivity if we consider the initial states which cannot be obtained as the partial trace of a correlated system-bath state formed after the fast relaxation process.

E. Mean-force Gibbs steady state

In the considered limit, the mean-force Gibbs state tends to

$$\rho_S^{(\text{st})} = Z_S^{-1} e^{-\beta \bar{H}_S^{(\text{d})}}, \quad Z_S = \text{Tr} e^{-\beta \bar{H}_S^{(\text{d})}}. \quad (114)$$

Let us prove that this state is stationary for the master equation derived in the previous section if we apply the secular approximation (also described in the end of the previous section). Denote the corresponding generators $\mathcal{R}_n^{(\text{sec})}$ and $\mathcal{T}_{nm}^{(\text{sec})}$.

The projection of state (114) onto the subspace $\mathcal{H}_S^{(n)}$ gives

$$\Pi_n \rho_S^{(\text{st})} \Pi_n = Z_S^{-1} e^{-\beta \bar{H}_S^{(n)}}, \quad (115)$$

i.e., the Gibbs state with respect to $\bar{H}_S^{(n)}$ (up to a normalization constant). It is well known to be stationary for the secular Redfield generator $\mathcal{R}_n^{(\text{sec})}$. So, it suffices to prove the stationarity of state (114) for the transition part $\sum \mathcal{T}_{nm}^{(\text{sec})}$ of the generator.

Since $[A_{\alpha nm\omega}^\dagger A_{\alpha nm\omega}, \bar{H}_S^{(\text{d})}] = 0$, state (114) commutes with the Lamb-shift Hamiltonian (107) in the secular approximation. Now establish the detailed balance conditions

$$\gamma_{\alpha\beta nm}(\omega) = \gamma_{\beta\alpha mn}(-\omega) e^{\beta\omega}, \quad (116)$$

where

$$\begin{aligned} \gamma_{\alpha\beta nm}(\omega) &\equiv \gamma_{\alpha\beta nm}(\omega, \omega) \\ &= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle e^{iH_B^{(m)}\tau} B_\alpha e^{-iH_B^{(n)}\tau} B_\beta \rangle_m. \end{aligned} \quad (117)$$

As in Sec. III D, let us change the variable of integration in Eq. (117) by $s = -\tau - i\beta$:

$$\begin{aligned} \gamma_{\alpha\beta nm}(\omega) &= e^{\beta\omega} \int_{-\infty}^{\infty} d\tau e^{-i\omega s} \langle e^{-iH_B^{(m)}s} B_\alpha e^{iH_B^{(n)}s} e^{-\beta H_B^{(n)}} B_\beta e^{\beta H_B^{(m)}} \rangle_m. \end{aligned}$$

Now applying Eq. (35), we obtain

$$\begin{aligned} \gamma_{\alpha\beta nm}(\omega) &= e^{\beta\omega} \int_{-\infty}^{\infty} d\tau e^{-i\omega s} \langle e^{-iH_B^{(m)}s} B_\alpha e^{iH_B^{(n)}s} (e^{-\beta H_B^{(n)}} B_\beta e^{\beta H_B^{(m)}}) \rangle_n. \end{aligned}$$

Now we apply the Kubo-Martin-Schwinger condition

$$\langle Y (e^{-\beta H_B^{(n)}} X e^{\beta H_B^{(n)}}) \rangle_n = \langle XY \rangle_n \quad (118)$$

for $Y = e^{-iH_B^{(m)}s} B_\alpha e^{iH_B^{(n)}s}$ and $X = B_\beta$, which gives

$$\begin{aligned} \gamma_{\alpha\beta nm}(\omega) &= e^{\beta\omega} \int_{-\infty}^{\infty} d\tau e^{-i\omega s} \langle B_\beta e^{-iH_B^{(m)}s} B_\alpha e^{iH_B^{(n)}s} \rangle_n \\ &= e^{\beta\omega} \int_{-\infty}^{\infty} d\tau e^{-i\omega s} \langle e^{iH_B^{(n)}s} B_\beta e^{-iH_B^{(m)}s} B_\alpha \rangle_n \\ &= \gamma_{\beta\alpha mn}(-\omega) e^{\beta\omega}. \end{aligned}$$

Now, in view of this detailed balance condition and

$$A_{\beta nm\omega} \rho_S^{(\text{st})} = \rho_S^{(\text{st})} A_{\beta nm\omega} e^{-\beta\omega}, \quad (119)$$

the terms

$$\gamma_{\alpha\beta nm}(\omega) A_{\beta nm\omega} \rho_S^{(\text{st})} A_{\alpha nm\omega}^\dagger$$

from $\mathcal{T}_{nm}^{(\text{sec})}$ are canceled out with the terms

$$\frac{1}{2} \gamma_{\beta\alpha mn}(-\omega) \{ A_{\beta mn, -\omega}^\dagger A_{\alpha mn, -\omega}, \rho_S^{(\text{st})} \}$$

from $\mathcal{T}_{mn}^{(\text{sec})}$ (note that $A_{\beta mn, -\omega}^\dagger = A_{\beta nm\omega}$), which proves the stationarity of the mean-force Gibbs state $\rho_S^{(\text{st})}$.

F. Off-diagonal blocks

We have derived equations for the diagonal blocks $\rho_S^{(\text{d})}$. The off-diagonal blocks (coherences) can be calculated by a slight generalization of the methods of Sec. IV. Denote

$$\begin{aligned}\rho_{nm}(t) &= \Pi_n \text{Tr}_B \{e^{-iH_0 t} \rho(t) e^{iH_0 t}\} \Pi_m \\ &= \Pi_n \text{Tr}_B \{e^{-iH_0 t} \mathcal{Q} \rho(t) e^{iH_0 t}\} \Pi_m,\end{aligned}\quad (120)$$

where again $\mathcal{Q} = 1 - \mathcal{P}$. If $\rho(0) = \mathcal{P} \rho(0)$, the substitution of Eq. (A5) gives

$$\rho_{nm}(t) = -i \int_0^t d\tau \Pi_n \text{Tr}_B \{e^{-iH_0 t} \mathcal{L}'(t-\tau) \mathcal{P} \rho(t-\tau) e^{iH_0 t}\} \Pi_m.$$

Again, we can substitute here $\rho(t-\tau)$ by $\rho(t)$ and obtain

$$\begin{aligned}\rho_{nm}(t) &= -i \int_0^t d\tau \Pi_n \text{Tr}_B \{e^{-iH_0 t} \mathcal{L}'(t-\tau) \mathcal{P} \rho(t) e^{iH_0 t}\} \Pi_m \\ &= i \sum_{\alpha=0}^M \sum_{\omega \in \mathcal{F}_{nm}} \int_0^t d\tau e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n - \omega)\tau} \\ &\times [\zeta_{0\alpha nm}^*(\tau) \rho_S^{(n)}(t) A_{\alpha nm\omega} - \zeta_{0\alpha nm}(\tau) A_{\alpha nm\omega} \rho_S^{(m)}(t)].\end{aligned}\quad (121)$$

The limit $t \rightarrow \infty$ and the substitution of $\rho_S^{(n)}(t)$ by the stationary operators $Z_S^{-1} e^{-\beta \tilde{H}_S^{(n)}}$ give the steady-state off-diagonal parts and, thus, correction to the steady-state obtained in the previous section.

The nonequilibrium corrections to coherences and the influence of initial coherences also can be calculated analogously to Sec. IV.

G. Degenerate ultrastrong coupling

For the explicit evaluation of both the rate constants $\Gamma_{\alpha\beta nm}(\omega)$ [Eq. (111)] and the coherences [Eq. (121)], we need explicit expressions for the functions $\zeta_{\alpha\beta nm}(\tau)$. For the case of the Förster and modified Redfield theories, they are derived in Refs. [35,37,40] using the cumulant expansion method (which we also use in Appendix B). The calculation for the considered general case is completely analogous. It is straightforward, but cumbersome.

For simplicity, we restrict our consideration to the case when Π_n are eigenprojectors of A_α , i.e., there is no off-diagonal part (86b) of H_I . In other words,

$$H' = V + \sum_n H_I^{(n)}. \quad (122)$$

This case can be qualified as the degenerate ultrastrong coupling combined with the weak coupling inside the subspaces. This case includes (but not limited to) a hybrid Förster-Redfield theory, see Sec. VC1. In this case, we need only the functions $\zeta_{00 nm}(\tau) \equiv \zeta_{nm}(\tau)$, which have been already evaluated in Eq. (41). The expressions generators \mathcal{T}_{nm} of the

master equation (99) can be simplified to:

$$\begin{aligned}\mathcal{T}_{nm} \rho_S &= -i[H_{\text{LS}}^{(nm)}, \rho_S] + \sum_{\omega, \omega' \in \mathcal{F}_{nm}} e^{i(\omega' - \omega)t} \\ &\times \gamma_{nm}(\omega) \left(V_{nm\omega} \rho_S V_{nm\omega'}^\dagger - \frac{1}{2} \{V_{nm\omega}^\dagger V_{nm\omega}, \rho_S\} \right),\end{aligned}\quad (123)$$

where

$$H_{\text{LS}}^{(nm)} = \sum_{\omega, \omega' \in \mathcal{F}_{nm}} e^{i(\omega' - \omega)t} S_{nm}(\omega, \omega') V_{nm\omega'}^\dagger V_{nm\omega}, \quad (124)$$

$$\gamma_{nm}(\omega, \omega') = \Gamma_{nm}(\omega) + \Gamma_{nm}^*(\omega'),$$

$$S_{nm}(\omega, \omega') = \frac{1}{2i} [\Gamma_{nm}(\omega) - \Gamma_{nm}^*(\omega')], \quad (125)$$

$$\Gamma_{nm}(\omega) = \int_0^\infty \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n - \omega)\tau} d\tau. \quad (126)$$

If we further adopt the secular approximation, then only the terms with $\omega' = \omega$ are present:

$$\begin{aligned}\gamma_{nm}(\omega, \omega) &\equiv \gamma_{nm}(\omega) = 2 \operatorname{Re} \Gamma_{nm}(\omega) \\ &= \int_{-\infty}^{+\infty} \zeta_{nm}(\tau) e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n - \omega)\tau} d\tau,\end{aligned}\quad (127)$$

$$S_{nm}(\omega, \omega) \equiv S_{nm}(\omega) = \operatorname{Im} \Gamma_{nm}(\omega). \quad (128)$$

Finally,

$$\begin{aligned}\rho_{nm}(t) &= i \sum_{\omega \in \mathcal{F}_{nm}} \int_0^t d\tau e^{i(\bar{\varepsilon}_m - \bar{\varepsilon}_n - \omega)\tau} [\zeta_{nm}^*(\tau) \rho_S^{(n)}(t) V_{nm\omega} \\ &- \zeta_{nm}(\tau) V_{nm\omega} \rho_S^{(m)}(t)].\end{aligned}\quad (129)$$

VI. CONCLUSIONS

We have introduced a regime of evolution of open quantum systems called the strong-decoherence regime. It includes the ultrastrong-coupling regime as an important particular case. We have derived the corresponding quantum master equations and their steady states, which are equal to the mean-force Gibbs state in the corresponding limit. Also, we have obtained the first-order corrections to these expressions for the steady states.

This formalism can be used for testing theories of strong-coupling quantum thermodynamics [5,95]. The thermodynamics of pure decoherence was proposed recently [47,48]. The strong-decoherence approximation can be regarded as a correction to pure decoherence: the strong pure decoherence complemented by the slow transfer between the subspaces.

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APPENDIX A: SOME FORMULAS OF THE PROJECTION OPERATOR FORMALISM

Denote $\mathcal{L} = [H, \cdot]$, where $H = H_0 + H'$ is a Hamiltonian, $\mathcal{L}_0 = [H_0, \cdot]$, $\mathcal{L}' = [H', \cdot]$, and $\mathcal{L}'(t) = [H'(t), \cdot]$, where $H'(t) = e^{iH_0 t} H' e^{-iH_0 t}$. Let also a projection (super)operator \mathcal{P} satisfy $[\mathcal{P}, \mathcal{L}_0] = 0$ and $\mathcal{P}\mathcal{L}'\mathcal{P} = 0$. Denote also $\mathcal{Q} = 1 - \mathcal{P}$. The von Neumann equation for the density operator $\rho(t)$ in the interaction representation with respect to H_0 is

$$\dot{\rho}(t) = -i\mathcal{L}'(t)\rho(t). \quad (\text{A1})$$

This is equivalent to the following system of equations:

$$\mathcal{P}\dot{\rho}(t) = -i\mathcal{P}\mathcal{L}'(t)\mathcal{Q}\rho(t), \quad (\text{A2a})$$

$$\mathcal{Q}\dot{\rho}(t) = -i\mathcal{L}'(t)\mathcal{P}\rho(t) - i\mathcal{Q}\mathcal{L}'(t)\mathcal{Q}\rho(t), \quad (\text{A2b})$$

If we treat $\mathcal{P}\rho(t)$ as a known function, then a formal solution of equation (A2b) for $\mathcal{Q}\rho(t)$ is

$$\mathcal{Q}\rho(t) = T_+ \exp \left\{ -i \int_0^t \mathcal{Q}\mathcal{L}'(\tau) d\tau \right\} \mathcal{Q}\rho(0) - i \int_0^t d\tau T_+ \exp \left\{ -i \int_\tau^t \mathcal{Q}\mathcal{L}'(\tau') d\tau' \right\} \mathcal{L}'(\tau) \mathcal{P}\rho(\tau), \quad (\text{A3})$$

where

$$T_+ \exp \left\{ -i \int_0^t f(\tau) d\tau \right\} = 1 + \sum_{n=1}^{\infty} (-i)^n \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n f(\tau_1) f(\tau_2) \cdots f(\tau_n) \quad (\text{A4})$$

is the chronological exponential. In particular, if $\mathcal{Q}\rho(0) = 0$, then, in the first order with respect to $\mathcal{L}'(t)$, we have

$$\mathcal{Q}\rho(t) = -i \int_0^t \mathcal{L}'(\tau) \mathcal{P}\rho(\tau) d\tau = -i \int_0^t \mathcal{L}'(t-\tau) \mathcal{P}\rho(t-\tau) d\tau. \quad (\text{A5})$$

Its substitution into Eq. (A2a) gives

$$\mathcal{P}\dot{\rho}(t) = - \int_0^t d\tau \mathcal{P}\mathcal{L}'(t) \mathcal{L}'(t-\tau) \mathcal{P}\rho(t-\tau). \quad (\text{A6})$$

The Markovian approximation is the replacement $\mathcal{P}\rho(t-\tau)$ by $\mathcal{P}\rho(t)$ and the extension of the upper limit of integration in Eq. (A6) to infinity. Both replacements means that the integrand quickly decays with τ [much faster than the rate of the evolution of $\mathcal{P}\rho(t-\tau)$]. Thus, we have Eq. (29):

$$\mathcal{P}\dot{\rho}(t) = - \int_0^\infty d\tau \mathcal{P}\mathcal{L}'(t) \mathcal{L}'(t-\tau) \mathcal{P}\rho(t). \quad (\text{A7})$$

If $\mathcal{Q}\rho(0) \neq 0$, then formula (A5) should be modified:

$$\mathcal{Q}\rho(t) = \mathcal{Q}\rho(0) - i \int_0^t \mathcal{Q}\mathcal{L}'(t-\tau) \mathcal{Q}\rho(0) d\tau - i \int_0^t \mathcal{L}'(t-\tau) \mathcal{P}\rho(t-\tau) d\tau, \quad (\text{A8})$$

if we take the first-order approximation to the first chronological exponential in Eq. (A3). Substitution of Eq. (A8) to Eq. (A2a) gives the master equation for $\mathcal{P}\rho(t)$ with inhomogeneous terms:

$$\mathcal{P}\dot{\rho}(t) = - \int_0^\infty d\tau \mathcal{P}\mathcal{L}'(t) \mathcal{L}'(t-\tau) [\mathcal{P}\rho(t) + \mathcal{Q}\rho(0)] - i\mathcal{P}\mathcal{L}'(t)\mathcal{Q}\rho(0). \quad (\text{A9})$$

APPENDIX B: CALCULATION OF THE RATE CONSTANTS

Here we adopt known calculations for the Förster and modified Redfield theories (see Refs. [35,37,40]) for our case. Let us derive formula (41). We have

$$\begin{aligned} H_B^{(n)} &= H_B + \delta\varepsilon_n + \sum_{\alpha} \theta_{\alpha n} B_{\alpha} \\ &= H_B^{(m)} + \delta\varepsilon_n - \delta\varepsilon_m + \sum_{\alpha} (\theta_{\alpha n} - \theta_{\alpha m}) B_{\alpha} \\ &= H_B^{(m)} + \delta\varepsilon_n - \delta\varepsilon_m + \sum_{\alpha} (\theta_{\alpha n} - \theta_{\alpha m}) \left[B_{\alpha}^{(m)} - \sum_{\beta} \theta_{\beta m} (\delta\varepsilon_{\alpha\beta} + \delta\varepsilon_{\beta\alpha}) \right] \\ &= H_B^{(m)} + \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) \delta\varepsilon_{\alpha\beta} + \sum_{\alpha} (\theta_{\alpha n} - \theta_{\alpha m}) B_{\alpha}^{(m)}, \end{aligned} \quad (\text{B1})$$

where the displaced operators $B_\alpha^{(m)}$ were defined in Eq. (87). Thus,

$$\langle e^{iH_B^{(m)}t} e^{-iH_B^{(m)}t} \rangle_m = \left\langle e^{iH_B^{(m)}t} \exp \left\{ -it \left[H_B^{(m)} + \sum_\alpha (\theta_{\alpha n} - \theta_{\alpha m}) B_\alpha^{(m)} \right] \right\} \right\rangle_m \times \exp \left\{ -it \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) \delta g_{\alpha\beta} \right\}. \quad (\text{B2})$$

The first factor can be calculated using the second-order cumulant (Magnus) expansion with respect to $B_\alpha^{(m)}$, which is exact for the bosonic bath due to Wick's theorem [45]. Since

$$\exp \left\{ -it \left[H_B^{(m)} + \sum_\alpha (\theta_{\alpha n} - \theta_{\alpha m}) B_\alpha^{(m)} \right] \right\} = e^{-iH_B^{(m)}t} \times T_+ \exp \left\{ -i \sum_\alpha (\theta_{\alpha n} - \theta_{\alpha m}) \int_0^t B_\alpha^{(m)}(\tau) d\tau \right\}, \quad (\text{B3})$$

where

$$B_\alpha^{(m)}(\tau) = e^{iH_B^{(m)}\tau} B_\alpha^{(m)} e^{-iH_B^{(m)}\tau}, \quad (\text{B4})$$

and T_+ is the chronological exponential (A4), and in view of $\langle B_\alpha^{(m)}(\tau) \rangle_m = 0$, the second-order cumulant expansion for the first factor in Eq. (B2) gives

$$\begin{aligned} \left\langle e^{iH_B^{(m)}t} \exp \left\{ -it \left[H_B^{(m)} + \sum_\alpha (\theta_{\alpha n} - \theta_{\alpha m}) B_\alpha^{(m)} \right] \right\} \right\rangle_m &= \left\langle T_+ \exp \left\{ -i \sum_\alpha (\theta_{\alpha n} - \theta_{\alpha m}) \int_0^t B_\alpha^{(m)}(\tau) d\tau \right\} \right\rangle_m \\ &= \exp \left[- \sum_{\alpha\beta} (\theta_{\alpha n} - \theta_{\alpha m})(\theta_{\beta n} - \theta_{\beta m}) g_{\alpha\beta}(t) \right], \end{aligned} \quad (\text{B5})$$

thus proving Eq. (41). We have used

$$\langle B_\alpha^{(m)}(t) B_\beta^{(m)} \rangle_m = \langle B_\alpha(t) B_\beta \rangle,$$

where $\langle \cdot \rangle$ denotes the average with respect to ρ_B (see Sec. II), and

$$B_\alpha(t) = e^{iH_B t} B_\alpha e^{-iH_B t}. \quad (\text{B6})$$

Now let us derive formula (70). Since

$$e^{-i(H_B + \sum_\alpha \theta_{\alpha n} B_\alpha)t} = e^{-iH_B t} T_+ \exp \left\{ -i \sum_\alpha \theta_{\alpha n} \int_0^t B_\alpha(\tau) d\tau \right\}$$

and

$$e^{i(H_B + \sum_\alpha \theta_{\alpha n} B_\alpha)t} = T_- \exp \left\{ i \sum_\alpha \theta_{\alpha n} \int_0^t B_\alpha(\tau) d\tau \right\} e^{iH_B t},$$

where

$$T_- \exp \left\{ -i \int_0^t f(\tau) d\tau \right\} = 1 + \sum_{n=1}^{\infty} (-i)^n \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n f(\tau_n) \cdots f(\tau_2) f(\tau_1), \quad (\text{B7})$$

we can express $\zeta_{mn l}(t, \tau)$ as

$$\begin{aligned} \zeta_{mn l}(t, \tau) &= \left\langle T_- \exp \left\{ i \sum_\alpha \theta_{\alpha m} \int_0^t B_\alpha(s) ds \right\} \times T_+ \exp \left\{ -i \sum_\alpha \theta_{\alpha n} \int_0^t B_\alpha(s) ds \right\} \times T_- \exp \left\{ i \sum_\alpha \theta_{\alpha n} \int_0^{t-\tau} B_\alpha(s) ds \right\} \right. \\ &\quad \left. \times T_+ \exp \left\{ -i \sum_\alpha \theta_{\alpha l} \int_0^{t-\tau} B_\alpha(s) ds \right\} \right\rangle. \end{aligned}$$

Again, the second-order cumulant expansion gives the exact value of this expectation. It consists of the second-order cumulant expansions of the single chronological exponentials and expectation of the products of different first-order expansion terms. We have

$$\left\langle T_+ \exp \left\{ -i \sum_\alpha \theta_{\alpha n} \int_0^t B_\alpha(s) ds \right\} \right\rangle = \exp \left\{ - \sum_{\alpha, \beta} \theta_{\alpha n} \theta_{\beta n} g_{\alpha\beta}(t) \right\}, \quad (\text{B8a})$$

$$\left\langle T_- \exp \left\{ i \sum_\alpha \theta_{\alpha n} \int_0^t B_\alpha(s) ds \right\} \right\rangle = \exp \left\{ - \sum_{\alpha, \beta} \theta_{\alpha n} \theta_{\beta n} g_{\alpha\beta}^*(t) \right\}, \quad (\text{B8b})$$

Let us consider an expectation of a product of first-order expansion terms:

$$\begin{aligned} \left\langle \int_0^{t_1} B_\alpha(s_1) ds_1 \int_0^{t_2} B_\beta(s_2) ds_2 \right\rangle &= \int_0^{t_1} ds_1 \int_0^{t_2} ds_2 C_{\alpha\beta}(s_1 - s_2) = g_{\alpha\beta}(t_1) + \int_0^{t_1} ds_1 \int_{s_1}^{t_2} ds_2 C_{\alpha\beta}(s_1 - s_2) \\ &= g_{\alpha\beta}(t_1) + \int_0^{t_1} ds_1 \int_0^{t_2-s_1} ds_2 C_{\alpha\beta}(-s_2) \\ &= g_{\alpha\beta}(t_1) + \int_0^{t_2} ds_1 \int_0^{t_2-s_1} ds_2 C_{\alpha\beta}(-s_2) + \int_{t_2}^{t_1} ds_1 \int_0^{t_2-s_1} ds_2 C_{\alpha\beta}(-s_2). \end{aligned}$$

The second and the third terms can be transformed into

$$\int_0^{t_2} ds_1 \int_0^{s_1} ds_2 C_{\alpha\beta}(-s_2) = \int_0^{t_2} ds_1 \int_0^{s_1} ds_2 C_{\beta\alpha}^*(s_2) = g_{\beta\alpha}^*(t_2)$$

and

$$\int_0^{t_1-t_2} ds_1 \int_0^{-s_1} ds_2 C_{\alpha\beta}(-s_2) = \int_0^{t_1-t_2} ds_1 \int_0^{-s_1} ds_2 C_{\alpha\beta}(-s_2) - \int_0^{t_1-t_2} ds_1 \int_0^{s_1} ds_2 C_{\alpha\beta}(s_2) = -g_{\alpha\beta}(t_1 - t_2).$$

Thus,

$$\left\langle \int_0^{t_1} B_\alpha(s_1) ds_1 \int_0^{t_2} B_\beta(s_2) ds_2 \right\rangle = h_{\alpha\beta}(t_1, t_2) \equiv g_{\alpha\beta}(t_1) - g_{\alpha\beta}(t_1 - t_2) + g_{\beta\alpha}^*(t_2). \quad (\text{B9})$$

We have

$$\begin{aligned} \zeta_{mn}(t, \tau) &= \exp \left\{ - \sum_{\alpha\beta} \theta_{\alpha m} \theta_{\beta n} g_{\alpha\beta}(t) - \sum_{\alpha\beta} \theta_{\alpha n} \theta_{\beta m} [g_{\alpha\beta}^*(t) - g_{\alpha\beta}(t - \tau)] - \sum_{\alpha\beta} \theta_{\alpha l} \theta_{\beta l} g_{\alpha\beta}(t - \tau) \right. \\ &\quad + \sum_{\alpha\beta} \theta_{\alpha m} \theta_{\beta n} [h_{\alpha\beta}(t, t) - h_{\alpha\beta}(t, t - \tau)] + \sum_{\alpha\beta} \theta_{\alpha m} \theta_{\beta l} h_{\alpha\beta}(t, t - \tau) + \sum_{\alpha\beta} \theta_{\alpha n} \theta_{\beta n} h_{\alpha\beta}(t, t - \tau) \\ &\quad \left. + \sum_{\alpha\beta} \theta_{\alpha n} \theta_{\beta l} [h_{\alpha\beta}(t, t - \tau) - h_{\alpha\beta}(t - \tau, t - \tau)] \right\}, \end{aligned}$$

which, after the substitution of expression (B9) for $h_{\alpha\beta}$, gives Eq. (70).

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