Relationship between effective-Hamiltonian and effective-Liouvillian dynamics

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We report the results of a theoretical investigation of the formal relationship between effective-Hamiltonian and effective-Liouvillian dynamics. It is shown that there are some difficulties associated with the application of effective Hamiltonian dynamics to the modeling of spectral and temporal properties of quantum systems. More specifically, we provide a rigorous proof that effective-Liouvillian dynamics is not reducible to effective-Hamiltonian dynamics without discarding dynamical information about the interruption of certain phase coherences between the relevant and irrelevant parts of a system and the transfer of those phase coherences into phase coherences and excitations in the irrelevant part. It is shown that the discarded dynamical information makes a significant contribution to the frequency-dependent nonradiative decay rate for a simple model system.

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I. INTRODUCTION

Recently we found that effective-Hamiltonian and effective-Liouvillian treatments of the following two problems yield dramatically different results: (i) spontaneous emission of photons in a cold cavity [1] and (ii) nonradiative decay of an excited state coupled to a damped manifold [2]. The difference in the results obtained in these treatments suggested to us that there is some fundamental formal difference between effective-Hamiltonian and effective-Liouvillian dynamics.

Although effective-Hamiltonian dynamics has been the subject of many formal discussions [3] and is a commonly employed mesoscopic model [3(d),4], we have been unable to find anything in the literature for understanding the differences in the results obtained for the two aforementioned problems. With the aim of resolving these differences, we were prompted to undertake a theoretical investigation exploring the formal relationship between effective-Hamiltonian and effective-Liouvillian dynamics.

The results of our investigation are reported in this paper. We show that there are some difficulties associated with the application of effective-Hamiltonian dynamics to the modeling of spectral and temporal properties of quantum systems. More specifically, we provide a rigorous proof that effective-Liouvillian dynamics is not reducible to effective-Hamiltonian dynamics without discarding dynamical information about the interruption of certain phase coherences between the relevant and irrelevant parts of a system and the transfer of those coherences into phase coherences and excitations in the irrelevant part. It is shown that this discarded information makes a significant contribution to the frequency-dependent nonradiative decay rate for a simple model system.

II. EFFECTIVE-HAMILTONIAN DYNAMICS

In treating spectral and temporal properties of quantum systems, investigators often introduce a frequency-dependent Hamiltonian $\hat{\mathcal{H}}_{\text{eff}}(i\omega+\varepsilon)$ to characterize the dynamics of the relevant part of the system [3,4]. In general, $\hat{\mathcal{H}}_{\text{eff}}(i\omega+\varepsilon)$ may be written in the form

$$\hat{\mathcal{H}}_{\text{eff}}(i\omega+\varepsilon)=\hat{\mathcal{H}}-i\hbar\hat{\mathcal{R}}_{\mathcal{H}}(i\omega+\varepsilon)\ , \tag{2.1}$$

where $\hat{\mathcal{H}}=\hat{H}_{P_{\mathcal{H}}P_{\mathcal{H}}}$ and [5]

$$\hat{\mathcal{R}}_{\mathcal{H}}(i\omega+\varepsilon)=(1/\hbar^2)\hat{H}_{P_{\mathcal{H}}Q_{\mathcal{H}}}[(i\omega+\varepsilon)\hat{Q}_{\mathcal{H}}+(i/\hbar)\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}]^{-1}\hat{H}_{Q_{\mathcal{H}}P_{\mathcal{H}}}\ , \tag{2.2}$$

with $\hat{H}_{P_{\mathcal{H}}P_{\mathcal{H}}}=\hat{P}_{\mathcal{H}}\hat{H}\hat{P}_{\mathcal{H}}$, $\hat{H}_{P_{\mathcal{H}}Q_{\mathcal{H}}}=\hat{P}_{\mathcal{H}}\hat{H}\hat{Q}_{\mathcal{H}}$, $\hat{H}_{Q_{\mathcal{H}}P_{\mathcal{H}}}=\hat{Q}_{\mathcal{H}}\hat{H}\hat{P}_{\mathcal{H}}$, and $\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}=\hat{Q}_{\mathcal{H}}\hat{H}\hat{Q}_{\mathcal{H}}$.

The projection operators $\hat{P}_{\mathcal{H}}=\sum_{j_B}|\phi_{j_B}\rangle\langle\phi_{j_B}|$ and $\hat{Q}_{\mathcal{H}}=\sum_{k_U}|\phi_{k_U}\rangle\langle\phi_{k_U}|$ project onto the relevant and irrelevant parts of the dynamics embedded in the Hamiltonian $\hat{H}$. These operators satisfy the usual relations $\hat{P}_{\mathcal{H}}+\hat{Q}_{\mathcal{H}}=\hat{I}_{\mathcal{H}}$, $\hat{P}^2_{\mathcal{H}}=\hat{P}_{\mathcal{H}}$, $\hat{Q}^2_{\mathcal{H}}=\hat{Q}_{\mathcal{H}}$, and $\hat{P}_{\mathcal{H}}\hat{Q}_{\mathcal{H}}=\hat{Q}_{\mathcal{H}}\hat{P}_{\mathcal{H}}=\hat{0}_{\mathcal{H}}$, where $\hat{I}_{\mathcal{H}}$ is the identity operator and $\hat{0}_{\mathcal{H}}$ is the null operator.

For the case of reversible systems (systems characterized by a Hermitian Hamiltonian), the projection operator $\hat{P}_{\mathcal{H}}$ projects onto bound states $\{|\phi_{j_B}\rangle\}$ and $\hat{Q}_{\mathcal{H}}$ projects onto unbound states $\{|\phi_{k_U}\rangle\}$. Given this interpretation of the projection operators, the effective Hamiltonian $\hat{\mathcal{H}}_{\text{eff}}(i\omega+\varepsilon)$ is usually represented by the form [3(a),3(b)]

$$\hat{\mathcal{H}}_{\text{eff}}(i\omega)=\hat{H}+\hat{\Delta}_{\mathcal{H}}(i\omega)-(i/2)\hat{\Gamma}_{\mathcal{H}}(i\omega) \tag{2.3}$$

obtained by taking the double limit $\lim_{\varepsilon\to0^+}\lim_{V\to\infty}\hat{\mathcal{H}}_{\text{eff}}(i\omega+\varepsilon)$, where $\lim_{V\to\infty}$ denotes the infinite-volume limit. In the above, $\hat{\Gamma}_{\mathcal{H}}(i\omega)$ and $\hat{\Delta}_{\mathcal{H}}(i\omega)$ are the frequency-dependent damping and level shift operators [3(a),3(b),6]:

$$\hat{\Gamma}_{\mathcal{H}}(i\omega)=2\pi\hat{H}_{P_{\mathcal{H}}Q_{\mathcal{H}}}\delta(\hbar\omega\hat{Q}_{\mathcal{H}}+\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}})\hat{H}_{Q_{\mathcal{H}}P_{\mathcal{H}}} \tag{2.4}$$

and

$$\hat{\Delta}_{\mathcal{H}}(i\omega)=-\hat{H}_{P_{\mathcal{H}}Q_{\mathcal{H}}}\mathrm{P}(\hbar\omega\hat{Q}_{\mathcal{H}}+\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}})^{-1}\hat{H}_{Q_{\mathcal{H}}P_{\mathcal{H}}}\ , \tag{2.5}$$

where P denotes the principal part.

It follows from Eqs. (2.1) and (2.3) that the damping and level shift operators may be written as

$$\hat{\Gamma}_{\mathcal{H}}(i\omega)=2\hbar\hat{\mathcal{R}}^{H}_{\mathcal{H}}(i\omega) \tag{2.6}$$

and

$$\hat{\Delta}_{\mathcal{H}}(i\omega)=-i\hbar\hat{\mathcal{R}}^{A}_{\mathcal{H}}(i\omega)\ , \tag{2.7}$$

where $\hat{\mathcal{R}}^{H}_{\mathcal{H}}(i\omega)$ and $\hat{\mathcal{R}}^{A}_{\mathcal{H}}(i\omega)$ denote the Hermitian and anti-Hermitian parts, respectively, of the operator $\hat{\mathcal{R}}_{\mathcal{H}}(i\omega)=\lim_{\varepsilon\to 0+}\lim_{V\to\infty}\hat{\mathcal{R}}_{\mathcal{H}}(i\omega+\varepsilon)$. Since we have not imposed any symmetry restrictions on the Hamiltonian $\hat{H}$, Eqs. (2.6) and (2.7) apply to both reversible and irreversible systems. (The latter type of systems are characterized by non-Hermitian Hamiltonians.) Hence, we shall simply interpret $\{|\phi_{j_B}\rangle\}$ and $\{|\phi_{k_U}\rangle\}$ as the basis vectors for the relevant and irrelevant parts of the Hamiltonian $\hat{H}$, respectively.

III. EFFECTIVE-LIOUVILLIAN DYNAMICS

With the effective Hamiltonian $\hat{\mathcal{H}}_{\mathrm{eff}}(i\omega)$ at hand, investigators often introduce an effective Liouville operator $\hat{\hat{\mathcal{L}}}_{\mathrm{eff}}(i\omega)$ of the form [7]

$$\hat{\hat{\mathcal{L}}}_{\mathrm{eff}}(i\omega)=\hat{\hat{\mathcal{L}}}+\left[\frac{1}{\hbar}\right]\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega)-\left[\frac{i}{2\hbar}\right]\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega)\ , \tag{3.1}$$

where $\hat{\hat{\mathcal{L}}}=(1/\hbar)\hat{\hat{\mathcal{H}}}^{-}$ is the Liouville operator for the relevant part, i.e., the Liouville operator associated with $\hat{\mathcal{H}}=\hat{H}_{P_{\mathcal{H}}P_{\mathcal{H}}}$.

In the above, the superoperators $\hat{\hat{\mathcal{H}}}^{-}$, $\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega)$, and $\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega)$ are defined in such a way that $\hat{\hat{\mathcal{H}}}^{-}\hat{A}=[\hat{\mathcal{H}},\hat{A}]_{-}$, $\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega)\hat{A}=[\hat{\Gamma}_{\mathcal{H}}(i\omega),\hat{A}]_{+}$, and $\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega)\hat{A}=[\hat{\Delta}_{\mathcal{H}}(i\omega),\hat{A}]_{-}$ for any operator $\hat{A}$, where the $+$ $(-)$ has been used to denote a commutator (anticommutator). Of course, $\hat{A}\hat{\hat{\mathcal{H}}}^{-}=-\hat{\hat{\mathcal{H}}}^{-}\hat{A}$, $\hat{A}\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega)=\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega)\hat{A}$, and $\hat{A}\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega)=-\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega)\hat{A}$.

A straightforward application of projection-operator techniques [8,9] to the Liouville equation leads to the effective-Liouville operator

$$\hat{\mathcal{L}}_{\mathrm{eff}}(i\omega+\varepsilon)=\hat{\mathcal{L}}-i\hat{\mathcal{R}}_{\mathcal{L}}(i\omega+\varepsilon)\ , \tag{3.2}$$

where $\hat{\mathcal{L}}=\hat{L}_{P_{\mathcal{L}}P_{\mathcal{L}}}$ is the Liouville operator for the relevant part and

$$\hat{\mathcal{R}}_{\mathcal{L}}(i\omega+\varepsilon)=\hat{L}_{P_{\mathcal{L}}Q_{\mathcal{L}}}[(i\omega+\varepsilon)\hat{Q}_{\mathcal{L}}+i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}]^{-1}\hat{L}_{Q_{\mathcal{L}}P_{\mathcal{L}}}\ , \tag{3.3}$$

with $\hat{L}_{P_{\mathcal{L}}P_{\mathcal{L}}}=\hat{P}_{\mathcal{L}}\hat{L}\hat{P}_{\mathcal{L}}$, $\hat{L}_{P_{\mathcal{L}}Q_{\mathcal{L}}}=\hat{P}_{\mathcal{L}}\hat{L}\hat{Q}_{\mathcal{L}}$, $\hat{L}_{Q_{\mathcal{L}}P_{\mathcal{L}}}=\hat{Q}_{\mathcal{L}}\hat{L}\hat{P}_{\mathcal{L}}$, and $\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}=\hat{Q}_{\mathcal{L}}\hat{L}\hat{Q}_{\mathcal{L}}$.

The projection operators

$$\hat{P}_{\mathcal{L}}=\sum_{j_B,k_B}|N_{j_Bk_B})(N^{\dagger}_{j_Bk_B}| \tag{3.4}$$

and

$$\hat{Q}_{\mathcal{L}}=\sum_{j_B,k_U}[|N_{j_Bk_U})(N^{\dagger}_{j_Bk_U}|+|N_{k_Uj_B})(N^{\dagger}_{k_Uj_B}|]+\sum_{j_U,k_U}|N_{j_Uk_U})(N^{\dagger}_{j_Uk_U}| \tag{3.5}$$

project onto the relevant and irrelevant parts of the Liouville operator $\hat{L}$ corresponding to the Hamiltonian $\hat{H}$. These operators satisfy the relations $\hat{P}_{\mathcal{L}}+\hat{Q}_{\mathcal{L}}=\hat{I}_{\mathcal{L}}$, $\hat{P}^2_{\mathcal{L}}=\hat{P}_{\mathcal{L}}$, $\hat{Q}^2_{\mathcal{L}}=\hat{Q}_{\mathcal{L}}$, and $\hat{P}_{\mathcal{L}}\hat{Q}_{\mathcal{L}}=\hat{Q}_{\mathcal{L}}\hat{P}_{\mathcal{L}}=\hat{0}_{\mathcal{L}}$, where $\hat{0}_{\mathcal{L}}$ is the null operator and $\hat{I}_{\mathcal{L}}$ is the identity operator for the vector space spanned by the biorthornormal basis set $\{(N^{\dagger}_{j_ak_b}|, |N_{j_ak_b});\ a,b=B \text{ or } U\}$.

The right-hand vectors $\{|N_{j_ak_b});\ a,b=B \text{ or } U\}$ are vectors corresponding to the dyadic operators $\{\hat{N}_{j_ak_b}=|\phi_{j_a}\rangle\langle\phi_{k_b}|;\ a,b=B \text{ or } U\}$, where $\{|\phi_{j_B}\rangle, |\phi_{k_U}\rangle\}$ are the same set of orthonormal vectors used to construct the effective Hamiltonian given by Eq. (2.1). By construction, the vectors $\{(N^{\dagger}_{j_ak_b}|, |N_{j_ak_b});\ a,b=B$ or $U\}$ satisfy the orthonormality and closure relations $(N^{\dagger}_{j_ak_b}|N_{l_cm_d})=\delta_{j_a,l_c}\delta_{k_b,m_d}$ and $\hat{I}_{\mathcal{L}}=\sum_{a,b}\sum_{j_a,k_b}|N_{j_ak_b})(N^{\dagger}_{j_ak_b}|$, where $a,b,c,d=B$ or U. The components $(N^{\dagger}_{j_ak_b}|A)[(A^{\dagger}|N_{j_ak_b})]$ of the vector $|A)[(A^{\dagger}|]$ corresponding to the dynamical variable $\hat{A}[\hat{A}^{\dagger}]$ and the matrix elements $L(j_a,k_b;l_c,m_d)$ of the Liouville operator $\hat{L}$ are given by $(N^{\dagger}_{j_ak_b}|A)=\langle\phi_{j_a}|\hat{A}|\phi_{k_b}\rangle=A(j_a,k_b)$ $[(A^{\dagger}|N_{j_ak_b})=\langle\phi_{k_b}|\hat{A}^{\dagger}|\phi_{j_a}\rangle=A^*(j_a,k_b)]$ and $L(j_a,k_b;l_c,m_d)=(N^{\dagger}_{j_ak_b}|\hat{L}|N_{l_cm_d})$. Note that the inner product $(A|B)$ is defined by $(A|B)=\mathrm{Tr}\,\hat{A}\hat{B}$. Also, note that $(A^{\dagger}|=|A)^{\dagger}$.

In order to make a comparison between the effective-Liouvillian operators given by Eqs. (3.1) and (3.2), it is convenient to recast Eq. (3.2) in the superoperator form

$$\hat{\hat{\mathcal{L}}}_{\mathrm{eff}}(i\omega)=\hat{\hat{\mathcal{L}}}+\hat{\hat{\Delta}}_{\mathcal{L}}(i\omega)-(i/2)\hat{\hat{\Gamma}}_{\mathcal{L}}(i\omega)\ , \tag{3.6}$$

where $\hat{\hat{\Delta}}_{\mathcal{L}}(i\omega)$ and $\hat{\hat{\Gamma}}_{\mathcal{L}}(i\omega)$ are Hermitian operators defined by

$$\hat{\hat{\Gamma}}_{\mathcal{L}}(i\omega)=2\hat{\hat{\mathcal{R}}}^{H}_{\mathcal{L}}(i\omega) \tag{3.7}$$

and

$$\hat{\hat{\Delta}}_{\mathcal{L}}(i\omega)=-i\hat{\hat{\mathcal{R}}}^{A}_{\mathcal{L}}(i\omega)\ , \tag{3.8}$$

with $\hat{\hat{\mathcal{R}}}^{H}_{\mathcal{L}}(i\omega)$ and $\hat{\hat{\mathcal{R}}}^{A}_{\mathcal{L}}(i\omega)$ denoting the Hermitian and anti-Hermitian parts, respectively, of the operator $\hat{\hat{\mathcal{R}}}_{\mathcal{L}}(i\omega)$. In the above,

$$\hat{\hat{\mathcal{L}}}_{\mathrm{eff}}(i\omega)=\lim_{\varepsilon\to 0+}\lim_{V\to\infty}\hat{\mathcal{L}}_{\mathrm{eff}}(i\omega+\varepsilon)$$

and

$$\hat{\hat{\mathcal{R}}}_{\mathcal{L}}(i\omega)=\lim_{\varepsilon\to 0+}\lim_{V\to\infty}\hat{\hat{\mathcal{R}}}_{\mathcal{L}}(i\omega+\varepsilon)\ .$$

IV. RELATIONSHIP BETWEEN EFFECTIVE-HAMILTONIAN AND EFFECTIVE-LIOUVILLIAN DYNAMICS

Of particular interest is the relationship between the effective-Liouville operators given by Eqs. (3.1) and (3.6).

Clearly, their equivalence requires the following relations to hold:

$$\hat{\hat{\Gamma}}_{\mathcal{L}}(i\omega)=(1/\hbar)\hat{\hat{\Gamma}}^{+}_{\mathcal{H}}(i\omega) \tag{4.1}$$

and

$$\hat{\hat{\Delta}}_{\mathcal{L}}(i\omega)=(1/\hbar)\hat{\hat{\Delta}}^{-}_{\mathcal{H}}(i\omega) . \tag{4.2}$$

So let us turn our attention to establishing the conditions for the applicability of Eqs. (4.1) and (4.2).

The matrix element $\mathcal{K}_{\mathcal{L}}(j_B,k_B;j_B',k_B';i\omega+\varepsilon) =(N^{\dagger}_{j_Bk_B}|\hat{\mathcal{K}}_{\mathcal{L}}(i\omega+\varepsilon)|N_{j_B'k_B'})$ of the operator $\hat{\mathcal{K}}_{\mathcal{L}}(i\omega+\varepsilon)$ is simply the Fourier-Laplace transform of the time-correlation function

$$K_{\mathcal{L}}(j_B,k_B;j_B',k_B';t)=(N^{\dagger}_{j_Bk_B}|\hat{L}_{P_{\mathcal{L}}Q_{\mathcal{L}}}\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{L}_{Q_{\mathcal{L}}P_{\mathcal{L}}}|N_{j_B'k_B'}) . \tag{4.3}$$

Introducing the explicit forms for $\hat{L}_{P_{\mathcal{L}}Q_{\mathcal{L}}}=\hat{P}_{\mathcal{L}}\hat{L}\hat{Q}_{\mathcal{L}}$ and $\hat{L}_{Q_{\mathcal{L}}P_{\mathcal{L}}}=\hat{Q}_{\mathcal{L}}\hat{L}\hat{P}_{\mathcal{L}}$ into Eq. (4.3) and then evaluating the pertinent matrix elements of the Liouville operator $\hat{L}$, we find that

$$\begin{aligned}K_{\mathcal{L}}(j_B,k_B;j_B',k_B';t)=(1/\hbar^2)\sum_{m_U,m_U'}\{&\mathcal{H}(m_U,k_B)(N^{\dagger}_{j_Bm_U}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})\mathcal{H}(k_B',m_U')\\&-\mathcal{H}(m_U,k_B)(N^{\dagger}_{j_Bm_U}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})\mathcal{H}(m_U',j_B')\\&-\mathcal{H}(j_B,m_U)(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})\mathcal{H}(k_B',m_U')\\&+\mathcal{H}(j_B,m_U)(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})\mathcal{H}(m_U',j_B')\} .\end{aligned} \tag{4.4}$$

It is evident from Eq. (4.4) that the following four time-correlation functions contribute to $K_{\mathcal{L}}(j_B,k_B;j_B',k_B';t)$:

$$(N^{\dagger}_{j_Bm_U}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})=\mathrm{Tr}\hat{N}^{\dagger}_{j_Bm_U}\exp(-i\hat{\hat{L}}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{N}_{j_B'm_U'} , \tag{4.5}$$

$$(N^{\dagger}_{j_Bm_U}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})=\mathrm{Tr}\hat{N}^{\dagger}_{j_Bm_U}\exp(-i\hat{\hat{L}}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{N}_{m_U'k_B'} , \tag{4.6}$$

$$(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})=\mathrm{Tr}\hat{N}^{\dagger}_{m_Uk_B}\exp(-i\hat{\hat{L}}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{N}_{j_B'm_U'} , \tag{4.7}$$

and

$$(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})=\mathrm{Tr}\hat{N}^{\dagger}_{m_Uk_B}\exp(-i\hat{\hat{L}}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{N}_{m_U'k_B'} . \tag{4.8}$$

Since effective-Hamiltonian dynamics does not include information about phase-coherence transfer that is mediated by interactions within the manifold of relevant states and interactions between the relevant and irrelevant manifolds (see Fig. 1), it seems reasonable to assume that effective-Liouvillian dynamics is reducible to effective-Hamiltonian dynamics when we neglect this information in the projected Liouville operator $\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}$ by allowing $\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}\to\sum_{j_U,k_U}\sum_{j_U',k_U'}|N_{j_Uk_U})L(j_U,k_U;j_U',k_U')(N^{\dagger}_{j_U'k_U'}|$ [see Eq. (3.5)]. The elimination of this dynamical information is equivalent to making the replacement

$$\exp(-i\hat{\hat{L}}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)\hat{N}_{j_ak_b}\to\exp[-(i/\hbar)\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]\hat{N}_{j_ak_b}\exp[+(i/\hbar)\hat{H}^{\dagger}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t] , \tag{4.9}$$

where $\hat{H}^{\dagger}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}$ is the adjoint of the projected Hamiltonian $\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}$ appearing in effective-Hamiltonian dynamics.

Introducing the replacement given by Eq. (4.9) into Eqs. (4.5)–(4.8) and subsequently making use of the relations $\langle\phi_{j_B}|\exp[\pm(i/\hbar)\hat{H}^{\dagger}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]=\langle\phi_{j_B}|$ and $\exp[\pm(i/\hbar)\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]|\phi_{j_B}\rangle=|\phi_{j_B}\rangle$, we find that

$$(N^{\dagger}_{j_Bm_U}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})\to\delta_{j_B,j_B'}\langle\phi_{m_U'}|\exp[+(i/\hbar)\hat{H}^{\dagger}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]|\phi_{m_U}\rangle , \tag{4.10}$$

$$(N^{\dagger}_{j_Bm_U}|\exp(-\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})\to 0 , \tag{4.11}$$

$$(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{j_B'm_U'})\to 0 , \tag{4.12}$$

and

$$(N^{\dagger}_{m_Uk_B}|\exp(-i\hat{L}_{Q_{\mathcal{L}}Q_{\mathcal{L}}}t)|N_{m_U'k_B'})\to\delta_{k_B',k_B}\langle\phi_{m_U}|\exp[-(i/\hbar)\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]|\phi_{m_U'}\rangle . \tag{4.13}$$

Now introducing the replacements given by Eqs. (4.10)–(4.13) into Eq. (4.4), we obtain

$$K_{\mathcal{L}}(j_B,k_B;j_B',k_B';t)=K^*_{\mathcal{H}}(k_B,k_B';t)\delta_{j_B,j_B'}+K_{\mathcal{H}}(j_B,j_B';t)\delta_{k_B,k_B'} , \tag{4.14}$$

where

$$K_{\mathcal{H}}(j_B,j_B';t)=(1/\hbar^2)\langle\phi_{j_B}|\hat{H}_{P_{\mathcal{H}}Q_{\mathcal{H}}}\exp[-(i/\hbar)\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}}t]\hat{H}_{Q_{\mathcal{H}}P_{\mathcal{H}}}|\phi_{j_B'}\rangle .$$

$K_{\mathcal{H}}(k_B,k_B';t)$, is similarly defined.

The Fourier-Laplace transform of Eq. (4.14) yields

$$\mathcal{K}^H_{\mathcal{L}}(j_B,k_B;j_B',k_B';i\omega)=\mathcal{K}^H_{\mathcal{H}}(k_B',k_B;i\omega)\delta_{j_B,j_B'}+\mathcal{K}^H_{\mathcal{H}}(j_B,j_B';i\omega)\delta_{k_B,k_B'} \tag{4.15}$$

and

$$\mathcal{K}^A_{\mathcal{L}}(j_B,k_B;j_B',k_B';i\omega)=-\mathcal{K}^A_{\mathcal{H}}(k_B',k_B;i\omega)\delta_{j_B,j_B'}+\mathcal{K}^A_{\mathcal{H}}(j_B,j_B';i\omega)\delta_{k_B,k_B'} . \tag{4.16}$$

With the aid of the formal definitions of the operators $\hat{\hat{\Gamma}}_{\mathcal{L}}(i\omega)$, $\hat{\hat{\Delta}}_{\mathcal{L}}(i\omega)$, $\hat{\hat{\Gamma}}_{\mathcal{H}}(i\omega)$, and $\hat{\hat{\Delta}}_{\mathcal{H}}(i\omega)$, we find that Eqs. (4.15) and (4.16) lead to Eqs. (4.1) and (4.2), which enables us to pass from Eq. (3.6) to Eq. (3.1). Since there is no *a priori* reason to expect the replacements given by Eqs. (4.10)–(4.13) to be mathematical equalities, we conclude that effective-Hamiltonian dynamics is an approximation to effective-Liouvillian dynamics.

Clearly, the use of effective-Hamiltonian dynamics to compute frequency-dependent decay rates and to construct effective Liouville operators of the form given by Eq. (3.1) is tantamount to discarding dynamical information about phase-coherence transfer that is mediated by interactions within the manifold of relevant states and interactions between the relevant and irrelevant manifolds (see Fig. 1). Of course, effective-Hamiltonian dynamics does include information about phase-coherence transfer that is mediated by interactions within the manifold of irrelevant states (see Fig. 1).

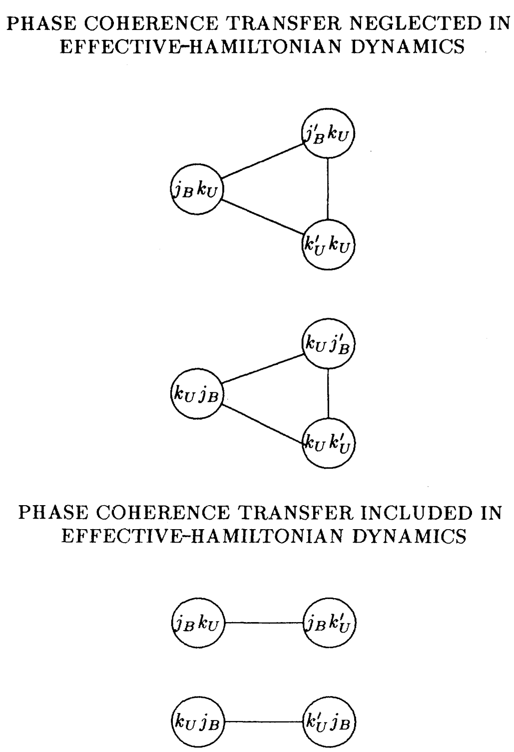

FIG. 1. Diagrams illustrating the phase-coherence transfers neglected and included in effective-Hamiltonian dynamics. The lines represent the interaction between the superstates enclosed in the circles. All of the displayed phase-coherence transfers are included in effective-Liouvillian dynamics.

The phase-coherence transfers neglected in effective-Hamiltonian dynamics vanish from effective-Liouville dynamics when the interactions within the relevant part and between the relevant and irrelevant parts vanish. This suggests that the effective Liouville operator given by Eq. (3.1) may be a good approximation to Eq. (3.6) for sufficiently weak interactions. Nonetheless, the neglected phase-coherence transfers may give rise to some interesting and important physical effects even when the interactions are weak [1,2].

V. ILLUSTRATIVE EXAMPLE

Now that we have discussed the relationship between effective-Hamiltonian and effective-Liouville dynamics, let us turn our attention to the comparison of these dynamics for an exactly solvable model. More specifically, we wish to determine the frequency-dependent nonradiative decay rate $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ for some radiatively damped excited state $|\phi_s\rangle$ that is coupled through the interaction $\hat{U}$ to some radiatively damped excited state $|\phi_l\rangle$. The states $|\phi_s\rangle$ and $|\phi_l\rangle$ are characterized by simple exponential radiative decay in the absence of the interaction $\hat{U}$. A schematic representation of the model is given in Fig. 2.

It follows from Eqs. (3.7) and (3.8) that

$$\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)=2\,\mathrm{Re}\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega) \tag{5.1}$$

and

$$\Delta_{\mathcal{L}}(s,s;s,s;i\omega)=\mathrm{Im}\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega) , \tag{5.2}$$

where

$\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega)=\lim_{\varepsilon\to 0^+}\lim_{V\to\infty}\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega+\varepsilon)$.

Exploiting the mathematical apparatus of dual Lanczos transformation theory [9,10], one can readily show that the exact result for $\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega+\varepsilon)$ may be written in the form of the continued fraction

$$\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega+\varepsilon)=\frac{2|U(s,l)|^2/\hbar}{\hbar(i\omega+\varepsilon)+d_+(s,l)+\dfrac{\Delta(s,l)}{\hbar(i\omega+\varepsilon)+d_+(s,l)-2d_-(s,l)|U(s,l)|^2/\Delta(s,l)-\dfrac{2d_-(s,l)^2|U(s,l)|^2\varepsilon(s,l)^2/\Delta(s,l)^2}{\hbar(i\omega+\varepsilon)+d_+(s,l)-d_-(s,l)\varepsilon(s,l)^2/\Delta(s,l)}}} \tag{5.3}$$

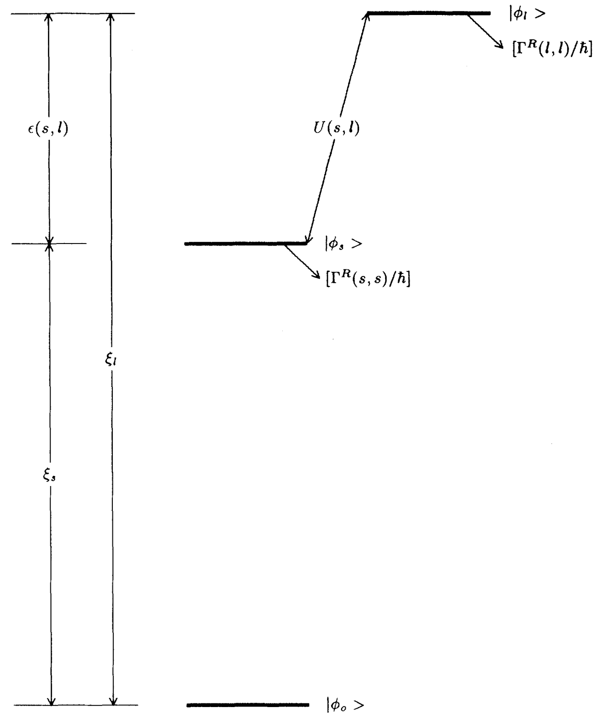

FIG. 2. Schematic representation of two coupled, radiatively damped excited states.

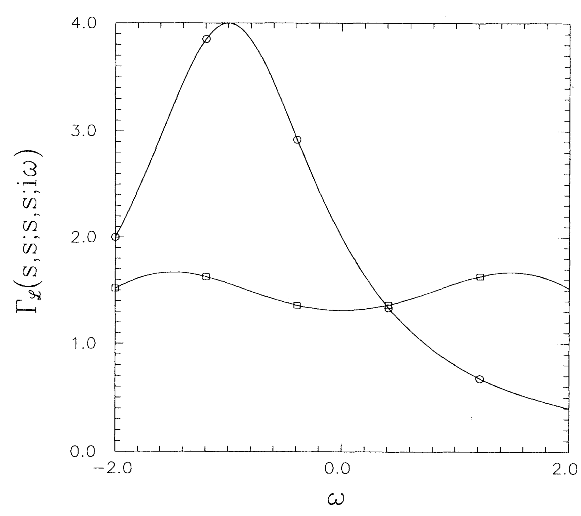

FIG. 3. Comparison of the exact results (□) for $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ with the approximate results (○) obtained by assuming the equivalence of the effective-Liouvillian and effective-Hamiltonian treatments. The displayed results are for the two-state system depicted in Fig. 2, with $\varepsilon(s,l)/\hbar=-1.0$, $|U(s,l)|/\hbar=1.0$, $\Gamma^R(s,s)/\hbar=0.5$, and $\Gamma^R(l,l)/\hbar=2.0$. For the effective-Hamiltonian treatment, $\varepsilon(s,l)=-\xi_l=1.0$.

or the rational function

$$\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega+\varepsilon)=[2|U(s,l)|^2/\hbar]\{[\hbar(i\omega+\varepsilon)+d_+(s,l)]^2-d_-(s,l)[\hbar(i\omega+\varepsilon)+d_+(s,l)]\}$$
$$\times\{[\hbar(i\omega+\varepsilon)+d_+(s,l)]^3-d_-(s,l)[\hbar(i\omega+\varepsilon)+d_+(s,l)]^2$$
$$+\Delta(s,l)[\hbar(i\omega+\varepsilon)+d_+(s,l)]-d_-(s,l)\varepsilon(s,l)^2\}^{-1}\ , \tag{5.4}$$

where $d_\pm(s,l)=\frac{1}{2}[\Gamma^R(s,s)\pm\Gamma^R(l,l)]$, $\varepsilon(s,l)=\xi_s-\xi_l$, and $\Delta(s,l)=2|U(s,l)|^2+\varepsilon(s,l)^2$, with $U(s,l)=\langle\phi_s|\hat{U}|\phi_l\rangle$.

It follows from Eqs. (2.6) and (2.7) that

$$\Gamma_{\mathcal{H}}(s,s;i\omega)=2\hbar\,\mathrm{Re}\mathcal{K}_{\mathcal{H}}(s,s;i\omega) \tag{5.5}$$

and

$$\Delta_{\mathcal{H}}(s,s;i\omega)=\hbar\,\mathrm{Im}\mathcal{K}_{\mathcal{H}}(s,s;i\omega)\ , \tag{5.6}$$

where $\mathcal{K}_{\mathcal{H}}(s,s;i\omega)=\lim_{\varepsilon\to 0+}\lim_{V\to\infty}\mathcal{K}_{\mathcal{H}}(s,s;i\omega+\varepsilon)$. One can readily show that

$$\mathcal{K}_{\mathcal{H}}(s,s;i\omega+\varepsilon)=\frac{(1/\hbar)|U(s,l)|^2}{\hbar(i\omega+\varepsilon)+\xi_l+\frac{1}{2}\Gamma^R(l,l)}\ . \tag{5.7}$$

From Eqs. (4.1) and (4.2), we see that the equivalence of the effective-Hamiltonian and effective-Liouvillian treatments requires the following equalities to hold:

$$\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)=(2/\hbar)\Gamma_{\mathcal{H}}(s,s;i\omega) \tag{5.8}$$

and

$$\Delta_{\mathcal{L}}(s,s;s,s;i\omega)=0\ . \tag{5.9}$$

These relations imply that

$$\mathrm{Re}\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega)=2\,\mathrm{Re}\mathcal{K}_{\mathcal{H}}(s,s;i\omega) \tag{5.10}$$

and

$$\mathrm{Im}\mathcal{K}_{\mathcal{L}}(s,s;s,s;i\omega)=0\ . \tag{5.11}$$

It is clear from Eqs. (5.3) and (5.7) that, in general, Eqs. (5.10) and (5.11) or, equivalently, Eqs. (5.8) and (5.9) do not hold. In fact, we see that these relations approximately hold only when

$$\frac{\Delta(s,l)}{\hbar(i\omega+\varepsilon)+d_+(s,l)-2d_-(s,l)|U(s,l)|^2/\Delta(s,l)-\dfrac{2d_-(s,l)^2|U(s,l)|^2\varepsilon(s,l)^2/\Delta(s,l)^2}{\hbar(i\omega+\varepsilon)+d_+(s,l)-d_-(s,l)\varepsilon(s,l)^2/\Delta(s,l)}}\simeq\varepsilon(s,l)^2\ , \tag{5.12}$$

$\xi_s=0$ or $\varepsilon(s,l)=-\xi_l$, and $\Gamma^R(s,s)=0$ or $d_+(s,l)=-d_-(s,l)=\frac{1}{2}\Gamma^R(l,l)$.

The approximation given by Eq. (5.12) is equivalent to assuming that $|U(s,l)|^2\ll\varepsilon(s,l)^2$. Nonetheless, the approximation $\xi_s=0$ or $\varepsilon(s,l)=-\xi_l$ is meaningless unless one assumes that the energy ξ_l is with respect to ξ_s.

Since there is no *a priori* reason to expect the above conditions to hold, we conclude that the effective-Hamiltonian treatment is not equivalent to the effective-Liouvillian treatment. For the two-state problem, we find that the effective-Hamiltonian treatment is only approximate due to the discarding of dynamical information about the phase-coherence transfer mediated by the interaction between the two states. This is illustrated in a concrete way in Figs. 3 and 4.

Upon inspection of Figs. 3 and 4, we see that the results based on the assumed equivalence of the effective-Hamiltonian and effective-Liouvillian treatments represent a rather poor approximation to the exact results for the effective-Liouvillian treatment. The approximate result for $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ exhibits a much stronger dependence on ω than the exact result (see Fig. 3). Moreover, the approximate result for $\Delta_{\mathcal{L}}(s,s;s,s;i\omega)$ vanishes for all ω, while the exact result assumes nonzero values for finite values of ω (see Fig. 4).

Agreement between the approximate and exact results is obtained only for a single frequency ω_A, differing for

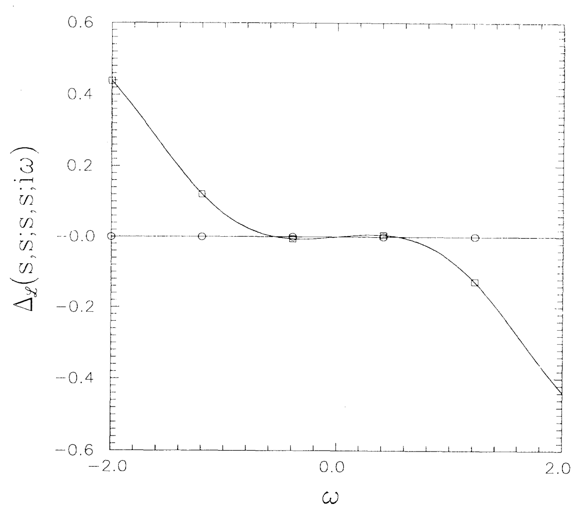

FIG. 4. Comparison of the exact results (□) for $\Delta_{\mathcal{L}}(s,s;s,s;i\omega)$ with the approximate results (○) obtained by assuming the equivalence of the effective-Liouvillian and effective-Hamiltonian treatments. The displayed results are for the two-state system depicted in Fig. 2, with $\varepsilon(s,l)/\hbar=-1.0$, $|U(s,l)|/\hbar=1.0$, $\Gamma^R(s,s)/\hbar=0.5$, and $\Gamma^R(l,l)/\hbar=2.0$. For the effective-Hamiltonian treatment, $\varepsilon(s,l)=-\xi_l=1.0$.

$\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ and $\Delta_{\mathcal{L}}(s,s;s,s;i\omega)$. For $\omega<\omega_A$, the approximate results overestimate $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$. For $\omega>\omega_A$, the approximate results underestimate $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$. Just the opposite behavior of the approximate results is realized for $\Delta_{\mathcal{L}}(s,s;s,s;i\omega)$.

Apart from the aforementioned difficulties with the approximate results based on the assumed equivalence of the effective-Hamiltonian and effective-Liouvillian treatments, we find that the approximate results do not reflect the correct symmetry of $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ with respect to ω. As can be seen from Fig. 3, the exact results for $\Gamma_{\mathcal{L}}(s,s;s,s;i\omega)$ are symmetric in ω. Since the approximate results for $\Delta_{\mathcal{L}}(s,s;s,s;i\omega)$ vanish for all ω, they obviously conform to the antisymmetric character of this quantity (see Fig. 4).

VI. CONCLUDING REMARKS

Difficulties inherent in the application of effective-Hamiltonian dynamics to the theoretical investigation of spectral and temporal properties of quantum systems were revealed. These difficulties were shown to arise from the neglect of phase-coherence transfer that is mediated by interactions within the manifold of relevant states and interactions between the relevant and irrelevant manifolds. In this paper, we have shown that the latter type of phase-coherence transfer is important for a simple two-state model. Elsewhere, we show that both types of phase-coherence transfer play an important role in the spontaneous emission of photons in a cold cavity [1] and the nonradiative decay of an excited state coupled to a damped manifold [2].

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[5] For the case of reversible systems, the operator $\hat{\mathcal{R}}_{\mathcal{H}}(i\omega+\varepsilon)$ is connected to the level shift operator $\hat{R}_{\mathcal{H}}(i\omega+\varepsilon)$ by the relation $\hat{R}_{\mathcal{H}}(i\omega+\varepsilon)=\hat{\mathcal{U}}-i\hbar\hat{\mathcal{R}}_{\mathcal{H}}(i\omega+\varepsilon)$, where $\hat{\mathcal{U}}$ is the interaction between bound states. See, for example, M. L. Goldberger and K. M. Watson, *Collision Theory* (Krieger, Huntington, 1975) for a discussion of the level shift operator.

[6] If we set $\hbar\omega=-\xi$ and replace the projection operator $\hat{Q}_{\mathcal{H}}$ in $(\hbar\omega\hat{Q}_{\mathcal{H}}+\hat{H}_{Q_{\mathcal{H}}Q_{\mathcal{H}}})$ with the identity operator $\hat{I}_{\mathcal{H}}$, the forms given by Eqs. (2.4) and (2.5) for $\hat{\Gamma}_{\mathcal{H}}(i\omega)$ and $\hat{\Delta}_{\mathcal{H}}(i\omega)$ assume the forms given by Feshbach and Messiah for the damping and level shift operators [see Refs. [3(a)] and [3(b)]]. Of course, Feshbach [see Ref. [3(a)]] interprets $\xi=-\hbar\omega$ as an energy variable due to the fact that he starts with the stationary eigenvalue problem $\hat{H}|\Psi\rangle=\xi|\Psi\rangle$ and then projects onto the bounded part $|\Psi^{P_{\mathcal{H}}}\rangle$ of $|\Psi\rangle$.

[7] See, for example, K. F. Freed, J. Chem. Phys. **64**, 1604 (1976); and Ref. [4(b)].

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