Interpolation between the Grover-Silbey and the generalized stochastic Liouville equation theories

V. Čápek and I. Barvík
Faculty of Mathematics and Physics, Institute of Physics of Charles University, Ke Karlovu 5, CS-121 16 Prague 2, Czechoslovakia
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A projection superoperator is introduced that is able to extract (from the full nonequilibrium exciton-phonon density matrix) the bare- as well as the dressed-exciton (exciton-polaron) single-particle density matrices. Applying it to a standard model of the exciton interacting, via a linear local coupling, with harmonic phonons in a linear chain, a general theory of exciton propagation is constructed. This theory well interpolates between the standard generalized stochastic Liouville equation (GSLE) approach and the Grover-Silbey (GS) theory [M. Grover and R. Silbey, J. Chem. Phys. **54**, 4843 (1971)] depending on an interpolation parameter determining details of the basis used. As this parameter (not connected with the model but depending just on our choice of the mathematical language used) can have no impact on the regime as well as the time dependence of the exciton propagation (measured by site occupation probabilities), all famous contradictions between GSLE (or stochastic Liouville equation) and GS approaches are interpreted as only formal and, in fact, seeming. This regards mainly the lack of the local γ_0 parameters and dependence of the γ_1 parameter on the exciton resonance integrals in the Grover-Silbey theory.

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I. INTRODUCTION

The microscopic theory of the exciton propagation under the influence of a quantum bath has existed in its detailed form since 1971, when Grover and Silbey (GS) published their (today almost classical) paper [1]. Though the approach containing elements of the canonical transformation theory (but in fact, avoiding this transformation) became quite popular, it became also quite often misinterpreted and so far has not been well understood in general. In order to illustrate this assertion, let us mention the problem of lacking [as compared to formally analogous equations of the stochastic Liouville equation (SLE) method by Primas [2], Haken and Strobl [3], and Reineker [4], derived in a completely different way] the γ_0 parameter describing (in the Haken-Strobl parametrization [3,4]) the influence of the local energy fluctuation on transversal relaxation and, via that, on the character of the exciton motion. This fact was noticed by Kenkre [5–7], but has never been well explained. The most popular explanation of the origin of the lack is that it is due to restriction, in the GS approach, to only a linear (in the lattice points displacements) exciton-phonon coupling. This interpretation became, however, clearly insufficient when Čápek [8] and Čápek and Szöcs [9] derived basic equations of the SLE method starting (as GS) from just the linear exciton-phonon coupling but refraining from substitution of the influence of the quantum phonons on the exciton by a classical stochastic potential field as in the SLE method. [This method, being physically more general as far as temperatures and nonperiodic systems are concerned, is sometimes called the generalized stochastic Liouville equation (GSLE) approach.] The final equations did, however, contain (in contrast to GS) the local energy fluctuation parameter γ_0. Another problem deserving attention regarding comparison of the GS and GSLE (or SLE) approaches is the pronounced dependence of the nonlocal γ_1 parameters on the exciton resonance (hopping) integrals in GS, but in contrast to that, full formal independence of these parameters on these integrals in SLE and GSLE approaches.

The paper is organized as follows. In order to show that these (seemingly serious) differences between the above two groups of theories are in fact (from the point of view of the exciton propagation problem and in the sense specified below) unphysical, we construct here a theory that (being dependent on a parameter of our choice, having in principle no impact on, e.g., the exciton site-occupation probabilities) interpolates between GS and GSLE theories. In the next section, basic notions and preliminary reasoning are given. In Sec. III, our theory (of the generalized master equation form) is constructed. Its interpolating character between GS and GSLE theories is discussed in Sec. IV. Conclusions can be then found in Sec. V.

II. PRELIMINARIES

For the sake of simplicity, we will work here with just a linear periodic chain containing one exciton. The reason is that extension of the present theory to more dimensional and complex systems is straightforward and brings no relevant additional information. Simultaneously, for simplicity only, we will treat just the case of a single molecule per elementary cell.

Our Hamiltonian then reads

$$\mathcal{H}=\mathcal{H}_{\rm ex}+\mathcal{H}_{\rm ph}+\mathcal{H}_{\rm ex\text{-}ph}\ , \tag{2.1}$$

where

$$\mathcal{H}_{\rm ex}=\sum_k \varepsilon(k)a_k^\dagger a_k=\sum_{\substack{m,n\\ m\neq n}} J_{mn}a_m^\dagger a_n \ ,$$

$$\varepsilon(k)=\sum_n J_{mn}e^{-ika(m-n)} \ , \tag{2.2a}$$

$$a_k=\frac{1}{\sqrt{N}}\sum_m a_m e^{-ikam} \ ,$$

$$\mathcal{H}_{\rm ph}=\sum_q \hbar\omega_q b_q^\dagger b_q \ , \tag{2.2b}$$

$$\mathcal{H}_{\text{ex-ph}}=\frac{1}{\sqrt{N}}\sum_{k,q} f(q)a_{k+q}^\dagger a_k(b_q+b_{-q}^\dagger) \tag{2.2c}$$

$$=\frac{1}{\sqrt{N}}\sum_{m,q} g_q e^{iqam}\hbar\omega_q a_m^\dagger a_m(b_q+b_{-q}^\dagger) \ ,$$

$$f(q)=\hbar\omega_q g_q \ .$$

Here J_{mn}, $\varepsilon(k)$, ω_q, and g_q are the exciton hopping (resonance) integral, corresponding exciton band energy, phonon frequency, and dimensionless exciton-phonon coupling constant, respectively. In, e.g., the transformation formulas from the localized-exciton (a_m) to the band-exciton annihilation operator [see (2.2a)], the combination am means position of the mth molecule, i.e., a is the lattice constant and m is an integer.

From the very beginning, the reader should be warned not to expect too much from our oversimplified Hamiltonian [(2.1) and (2.2)]. Its main drawback is, at first sight, the lack of the site off-diagonal exciton-phonon coupling. Thus our model is able to reproduce basic equations of the stochastic Liouville equation model (see the generalized stochastic Liouville equation theory in [8,9]) but in, e.g., the Haken-Strobl parametrization [3], it then necessarily yields (as will be also seen below) all the off-diagonal Haken-Strobl parameters equal to zero ($\gamma_{mn}=0$, $m\neq n$). This is certainly the simplest case that might induce attempts to generalize our treatment here to also include the site off-diagonal exciton-phonon coupling.

We do not do that for two reasons. First, technically, we simultaneously want to include, as in the opposite limiting case, the theory of Grover and Silbey [1], which was formulated just for the diagonal exciton-phonon coupling. The second reason is deeply physical. Wagner and Koengeter [10,11] have recently raised serious objections against the adiabatic approximation that is inherently connected with the adiabatic representation working with the basis of states of moving (vibrating, librating, etc.) molecules. The only alternative to this representation is that of the crude or rigid basis, where molecular states used to expand field operators are taken at, e.g., equilibrium nuclear coordinates (see, e.g., [12]). In this crude representation, exciton site off-diagonal terms in the Hamiltonian are solely owing to the electron-electron coupling (the only two-electron operator in the Hamiltonian), which is, however, fully independent of the nuclear displacements. So, no site off-diagonal exciton-phonon coupling term appears in the Hamiltonian in this representation.

Detailed discussion of the relation of the rigid basis and adiabatic basis formulations of the Hamiltonian can be found in [12]. Admittedly, while the adiabatic representation is handicapped technically (owing to the adiabatic approximation mentioned above), the rigid basis representation is handicapped physically. This makes it necessary to describe electronically unexcited molecular states with shifted (deformed or turned) nuclear skeletons via unshifted (undeformed or unturned) and electronically unexcited or (monoexcited as well as higher) excited states. The same applies to, e.g., moving electronically monoexcited states. So, formally, the exciton nonconservation may appear though the number of real excitations remains conserved. Some aspects of this phenomenon necessarily accompanying the crude (rigid basis) representation are discussed in [13]. Here, we will not deal with these complications in detail.

The standard approach to the problem given above is via a canonical transformation to the small polaron basis [1,14]. In accordance with GS [1], we introduce new exciton creation and annihilation operators

$$A_n=e^{-S}a_n e^{S} \ , \quad A_n^\dagger=e^{-S}a_n^\dagger e^{S} \ . \tag{2.3a}$$

Similarly, new phonon annihilation and creation operators read

$$B_q=e^{-S}b_q e^{S} \ , \quad B_q^\dagger=e^{-S}b_q^\dagger e^{S} \ , \tag{2.3b}$$

where

$$S=-S^\dagger=\frac{1}{\sqrt{N}}\sum_{q,n}\lambda g_q e^{iqan}a_n^\dagger a_n(b_{-q}^\dagger-b_q) \ . \tag{2.4}$$

Here λ is a new real parameter that remains to be specified. Clearly, this canonical transformation preserves the usual commutational relations. Let us also notice that from Eqs. (2.3a), (2.3b), and (2.4), one obtains

$$A_n=a_n\exp\left\{\frac{1}{\sqrt{N}}\sum_q \lambda g_q e^{iqan}(b_{-q}^\dagger-b_q)\right\}\equiv a_n\theta_n \ ,$$
$$B_q=b_q+\frac{1}{\sqrt{N}}\sum_n \lambda g_{-q}e^{-iqan}a_n^\dagger a_n \ . \tag{2.5}$$

Thus, e.g., $A_n^\dagger$ creates, in addition to the exciton in its center, a lattice polarization cloud, while $B_n^\dagger$ creates a phonon in the chain already deformed by the presence of the exciton. (The magnitude of these lattice effects depends, however, on the chosen value of λ, which remains still unspecified.) Therefore,

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1 \ , \tag{2.6a}$$

$$\mathcal{H}_0=\sum_{m,n}\left\{(1-\delta_{mn})J_{mn}\langle\theta_n^\dagger\theta_m\rangle+\delta_{mn}(\lambda^2-2\lambda)\frac{1}{N}\sum_q\hbar\omega_q|g_q|^2\right\}A_m^\dagger A_n$$
$$+\sum_q\hbar\omega_q B_q^\dagger B_q \ , \tag{2.6b}$$

$$\mathcal{H}_1=\frac{1}{\sqrt{N}}\sum_{q,n}\hbar\omega_q g_q(1-\lambda)e^{iqan}A_n^\dagger A_n(B_q+B_{-q}^\dagger)$$
$$+\sum_{\substack{m,n\\ m\neq n}}J_{mn}\{\theta_n^\dagger\theta_m-\langle\theta_n^\dagger\theta_m\rangle\}A_m^\dagger A_n\ , \tag{2.6c}$$

with

$$\theta_n=\exp\left\{N^{-1/2}\sum_q\lambda g_q e^{iqan}(B_q-B_{-q}^\dagger)\right\}$$
$$=\exp\left\{N^{-1/2}\sum_q\lambda g_q e^{iqan}(b_q-b_{-q}^\dagger)\right\}\ . \tag{2.7}$$

Consequently, as in GS [1] (and formally but not physically as in, e.g., [14], because we do not as a matter of fact apply the canonical transformation to $\mathcal{H}$ in contrast to [14]), we merely reexpress our (old) Hamiltonian $\mathcal{H}$ in terms of our new operators A, B, etc. For $\lambda=1$, the above transformation is the standard small polaron (dressed-exciton) one. For $\lambda=0$, no transformation to new operators $A,B,\ldots$ is performed. Thus for $\lambda\in\langle 0,1\rangle$ (though other values are not in principle excluded), we have an interpolation between the bare- and dressed (polaron)-exciton picture (i.e., the partially-dressed-exciton polaron). One should add here that the idea of the intermediate polaron transformation appeared in [15]. Let us add yet here that λ is still a free but unphysical parameter on which neither the energy spectrum nor the time dependence nor regime of the excitation transfer (as far as criteria for its determination are chosen as λ independent) depends. So, no unambiguous physical interpretation (as is usual when $\lambda=1$) should be given to, e.g., separate λ-dependent terms in (2.6a) or, for instance, to the energy spectrum of $\mathcal{H}_0$. [Notice that, e.g., the polaron shift, i.e., the second term in the parentheses in the first term in (2.6b), starts to increase when λ exceeds unity, which can hardly be well interpreted.]

In (2.6b) and (2.6c), $\langle\ \rangle$ designates as usual the thermal average (see, e.g., GS [1]) with respect to (2.6b). Direct calculation yields

$$\langle\theta_n^\dagger\theta_m\rangle=\exp\left[-N^{-1}\sum_q\lambda^2|g_q|^2\{1-\cos[qa(m-n)]\}\right.$$
$$\left.\times\coth(\beta\hbar\omega_q/2)\right]\ , \tag{2.8}$$

which again turns to the usual small-polaron exponential reducing, e.g., the small-polaron bandwidth (with respect to the bare-exciton bandwidth) when $\lambda=1$. Again, however, λ in (2.8) is in fact so far arbitrary and should thus not (as far as we were able to avoid approximations) enter physical conclusions.

The quantity of our interest is

$$\bar\rho_{mn}(t)\equiv\bar\rho_{mn}(\lambda,t)=\mathrm{Tr}[\rho(t)A_n^\dagger A_m]$$
$$=\mathrm{Tr}[\rho(0)A_n^\dagger(t)A_m(t)]\ , \tag{2.9}$$

where $\rho(t)$ is the total exciton-phonon density matrix. Clearly, $\bar\rho$ is (for general λ) the partially-dressed-exciton (single-particle) density matrix. For $\lambda=0$ or $\lambda=1$, it reduces to the bare (single-exciton density matrix or $\mathcal{G}_{nm}(t)$ parameters of Grover and Silbey [1], which thus form (up to the interchange of indices) nothing but the (fully) dressed (single)-exciton density matrix. Direct introduction of (2.3) yields

$$\bar\rho_{mn}(\lambda,t)=\mathrm{Tr}(\rho(t)\{a_n^\dagger a_m+[a_n^\dagger a_m,S]$$
$$+\tfrac{1}{2}[[a_n^\dagger a_m,S],S]+\cdots\})\ . \tag{2.10}$$

With S being given as in (2.4), one can easily verify that

$$P_m(t)=\bar\rho_{mm}(\lambda,t)=\mathrm{Tr}[\rho(t)A_m^\dagger A_m]=\mathrm{Tr}[\rho(t)a_m^\dagger a_m] \tag{2.11}$$

is λ independent providing the site-occupation probability of finding the exciton (bare for $\lambda=0$, partially dressed for $0<\lambda<1$, or dressed for $\lambda=1$) at site m. Please notice that we cannot exclude the possibility of the "overdressed" exciton for $\lambda>1$.) On the other hand, the off-diagonal elements $\bar\rho_{mn}(t)$, $m\neq n$ are (because then $[a_n^\dagger a_m,S]\neq 0$ in (2.10)) clearly λ dependent, which makes these elements different in, e.g., the generalized stochastic Liouville equation model (see, for instance, [8]) when $\lambda=0$ and in the Grover-Silbey theory [1] with $\lambda=1$.

III. GENERALIZED MASTER EQUATIONS

Assuming just one exciton in the system, we adapt our projector, which we choose in the form of the Čápek-Barvík [16] projector

$$D\cdots=\sum_{m,n}\mathrm{Tr}(A_m\cdots A_n^\dagger)A_m^\dagger\rho_0 A_n$$
$$=\sum_{k_1,k_2}\mathrm{Tr}(A_{k_1}\cdots A_{k_2}^\dagger)A_{k_1}^\dagger\rho_0 A_{k_2}\ , \tag{3.1a}$$

$$A_k=\frac{1}{\sqrt{N}}\sum_n A_n e^{-ikan}\ . \tag{3.1b}$$

In (3.1a), ρ_0 is an arbitrary operator with property $A_p\rho_0=\rho_0 A_q^\dagger=0$ [otherwise the identity $D^2=D$ would not necessarily be fulfilled, i.e., (3.1) would not have the idempotency property required for projectors]. We choose

$$\rho_0=|\mathrm{vac_{ex}}\rangle\langle\mathrm{vac_{ex}}|\otimes\frac{e^{-\beta H_{\mathrm{ph}}}}{\mathrm{Tr_{ph}}e^{-\beta H_{\mathrm{ph}}}} \tag{3.2}$$

here. Our projector D is then to be applied to either the Nakajima-Zwanzig [17–19] or Shibata-Hashitsume-Takahashi-Shingu [20,21] identity in order to obtain either the time-convolution or time-convolutionless generalized master equations (TC-GME or TCL-GME) for the reduced information provided by our projector D.

First, let us introduce

$$\tilde\rho(t)=e^{i\mathcal{H}_0 t/\hbar}\rho(t)e^{-i\mathcal{H}_0 t/\hbar}\equiv e^{i\mathcal{L}_0 t}\rho(t)\ . \tag{3.3}$$

Then

$$\frac{\partial}{\partial t}D\rho(t)=\sum_{m,n}A_m^\dagger\rho_0 A_n\frac{\partial}{\partial t}\mathrm{Tr}[A_m\rho(t)A_n^\dagger]$$
$$=\sum_{m,n}A_m^\dagger\rho_0 A_n\left\{\left[-\frac{i}{h}\right]\mathrm{Tr}(A_m[\mathcal{H}_0,\rho(t)]A_n^\dagger)+\sum_{r,s}(e^{-i\mathcal{L}_0 t})_{mnrs}\mathrm{Tr}\left[A_r\frac{\partial\tilde{\rho}(t)}{\partial t}A_s^\dagger\right]\right\}$$
$$=\left[-\frac{i}{h}\right]D[\mathcal{H}_0,\rho(t)]+\sum_{m,n}A_m^\dagger\rho_0 A_n\sum_{r,s}(e^{-i\mathcal{L}_0 t})_{mnrs}\mathrm{Tr}\left[A_r\frac{\partial\tilde{\rho}(t)}{\partial t}A_s^\dagger\right]. \tag{3.4}$$

A. TC-GME

The Nakajima-Zwanzig identity [17–19] reads in the interaction picture

$$\frac{\partial}{\partial t}D\tilde{\rho}(t)=-iD\mathcal{L}_1(t)D\tilde{\rho}(t)-\int_0^t D\mathcal{L}_1(t)\exp_{\leftarrow}\left\{-i\int_\tau^t(1-D)\mathcal{L}_1(\tau_1)d\tau_1\right\}(1-D)\mathcal{L}_1(\tau)D\tilde{\rho}(\tau)d\tau$$
$$-iD\mathcal{L}_1(t)\exp\left\{-i\int_{t_0}^t(1-D)\mathcal{L}_1(\tau)\right\}(1-D)\rho(0)\,, \tag{3.5a}$$

$$\mathcal{L}_1(t)=e^{i\mathcal{L}_0 t}\mathcal{L}_1 e^{-i\mathcal{L}_0 t}\,,\quad \mathcal{L}_1\cdots\equiv\frac{1}{\hbar}[\mathcal{H}_1,\ldots]\,. \tag{3.5b}$$

Thus we can calculate, using (3.5), term-by-term contributions to $(\partial/\partial t)\mathrm{Tr}(A_r\tilde{\rho}A_s^\dagger)$ on the right-hand side of (3.4). It is from (3.5) and (3.1a) to the second order in $\mathcal{L}_1$ (both GS [1] and SLE [2–4] or GSLE [8,9] are effectively second-order theories):

$$\sum_{m,n}A_m^\dagger\rho_0 A_n\mathrm{Tr}\left[A_m\frac{\partial\tilde{\rho}(t)}{\partial t}A_n^\dagger\right]=-\frac{i}{\hbar}\sum_{m,n,r,s}A_m^\dagger\rho_0 A_n\mathrm{Tr}\{A_m(e^{i\mathcal{L}_0 t}[\mathcal{H}_1,e^{-i\mathcal{L}_0 t}A_r^\dagger\rho_0 A_s])A_n^\dagger\}\mathrm{Tr}[A_r\rho(t)A_s^\dagger]$$
$$-\frac{1}{\hbar^2}\sum_{m,n}A_m^\dagger\rho_0 A_n\mathrm{Tr}\left[A_m\int_0^t\{e^{i\mathcal{L}_0 t}[\mathcal{H},e^{-i\mathcal{L}_0 t}(1-D)\mathcal{L}_1(\tau)]d\tau\}A_n^\dagger\right]. \tag{3.6}$$

Here, we have already omitted the last (initial condition) term on the right-hand side of (3.5a), assuming the initial condition

$$\rho(0)=A_0^\dagger\rho_0 A_0\,, \tag{3.7}$$

i.e.,

$$(1-D)\rho(0)=0\,. \tag{3.8}$$

One should realize that our initial condition (3.7) is λ dependent [i.e., $\rho(0)$ depends on our choice of λ], meaning that a partially (with degree given by λ) dressed exciton is initially created at site zero. This λ dependence should be kept in mind when comparing SLE and Grover-Silbey theories, in particular at short t.

It is

$$\mathrm{Tr}(A_m\{e^{i\mathcal{L}_0 t}[\mathcal{H}_1,(e^{-i\mathcal{L}_0 t}A_r^\dagger\rho_0 A_s)]\}A_n^\dagger)$$
$$=\mathrm{Tr}\{a_m[\mathcal{H}_1'(t),a_r^\dagger\rho_0 a_s]a_n^\dagger\}=0\,, \tag{3.9}$$

owing to the fact that

$$[\mathcal{H}_1',a_r^\dagger\rho_0 a_s]\propto(b_q+b_{-q}^\dagger)e^{-\beta H_{\mathrm{ph}}}\,, \tag{3.10}$$

which always yields zero when taking $\mathrm{Tr}_{\mathrm{ph}}$. In (3.9), we have introduced the operators $\mathcal{H}_0'$ and $\mathcal{H}_1'$ which are nothing but $\mathcal{H}_0$ and $\mathcal{H}_1$ in (2.6a) and (2.6b), with only $A_m^\dagger$, A_m, B_q, and $B_q^\dagger$ being substituted by $a_m^\dagger$, a_m, b_q, and $b_q^\dagger$, respectively.

Further, for similar reasons, one can replace the term $(1-D)$ in the commutator in the second term on the right-hand side of (3.6) by unity. Thus

$$\mathrm{Tr}\left[A_m\frac{\partial\tilde{\rho}}{\partial t}A_n^\dagger\right]$$
$$\approx-\frac{1}{\hbar^2}\sum_{r,s}\int_0^t dr\,\mathrm{Tr}\{A_m[\mathcal{H}_1(t),[\mathcal{H}_1(\tau),A_r^\dagger\rho_0 A_s]]A_n^\dagger\}$$
$$\times\mathrm{Tr}[A_r\tilde{\rho}(\tau)A_s^\dagger] \tag{3.11}$$

and (3.4) yields

$$\frac{\partial}{\partial t}\bar{\rho}_{mn}(t)\approx\left[-\frac{i}{h}\right]\sum_r[\tilde{J}_{mr}\bar{\rho}_{rn}(t)-\bar{\rho}_{mr}(t)\tilde{J}_{rn}]+\left[-\frac{1}{\hbar^2}\right]\sum_{p,q}\int_0^t dr\,\mathrm{Tr}(A_m e^{-i\mathcal{L}_0 t}[\mathcal{H}_1(t),[\mathcal{H}_1(\tau),A_p^\dagger\rho_0 A_q[\,]A_n^\dagger)\bar{\rho}_{pq}(\tau)$$

$$=\left[\frac{i}{\hbar}\right]\sum_r[\tilde{J}_{mr}\bar{\rho}_{rn}(t)-\bar{\rho}_{mr}(t)\tilde{J}_{rn}]+\left[-\frac{1}{\hbar^2}\right]\sum_{r,s}\int_0^t dr\,\mathrm{Tr}(A_m e^{-i\mathcal{L}_0 t}[\mathcal{H}_1(t),[\mathcal{H}_1(\tau),e^{i\mathcal{L}_0\tau}A_r^\dagger\rho_0 A_s]]A_n^\dagger)\bar{\rho}_{rs}(\tau)$$

$$\approx\left[-\frac{i}{\hbar}\right]\sum_r[\tilde{J}_{mr}\bar{\rho}_{rn}(t)-\bar{\rho}_{mr}(t)\tilde{J}_{rn}]+\left[-\frac{1}{\hbar^2}\right]\int_{-\infty}^0 d\tau\,\mathrm{Tr}(A_m[\mathcal{H}_1,[(e^{i\mathcal{L}_0\tau}\mathcal{H}_1),A_r^\dagger\rho_0 A_s]]A_n^\dagger)\bar{\rho}_{rs}(t)\ . \tag{3.12}$$

Here, in the third equality, we have employed the standard Markov approximation; further, the notation

$$\tilde{J}_{mn}=J_{mn}\langle\theta_n^\dagger\theta_m\rangle\equiv\tilde{J}_{mn}(\lambda) \tag{3.13}$$

[see (2.8)] has been used.

B. TCL-GME

We start from the Shibata-Hashitsume-Takahashi-Shingu identity [20,21] in the interaction picture

$$\frac{\partial}{\partial t}D\tilde{\rho}(t)=-iD\mathcal{L}_1(t)1+i\int_0^t\mathcal{G}(t,\tau)(1-D)\tilde{\mathcal{L}}(\tau)\times DG(t,\tau)d\tau^{-1}\times[D\tilde{\rho}(t)+\mathcal{G}(t,0)(1-D)\rho(0)]\ ,$$
$$\mathcal{G}(t,\tau)=\exp_{\leftarrow}\left[-i\int_\tau^t(1-D)\tilde{\mathcal{L}}_1(s)ds\right]\ ,\qquad G(t,\tau)=\exp_{\rightarrow}\left[i\int_\tau^t\mathcal{L}_1(s)ds\right]\ , \tag{3.14}$$

though other equivalent possibilities [22,23] are also available (compare [24]). In the second order in $\mathcal{L}_1$ and applying (3.1) with (3.8), we obtain (extending integrations to infinity)

$$\frac{\partial}{\partial t}\bar{\rho}_{mn}(t)\approx\left[-\frac{i}{\hbar}\right]\sum_r[\tilde{J}_{mn}\bar{\rho}_{rn}(t)-\bar{\rho}_{mr}(t)\tilde{J}_{rn}]+\left[-\frac{1}{\hbar^2}\right]\sum_{r,s}\int_{-\infty}^0 d\tau\,\mathrm{Tr}\{A_m[\mathcal{H}_1,[(e^{i\mathcal{L}_0\tau}\mathcal{H}_1),A_r^\dagger\rho_0 A_s]]A_n^\dagger\}\bar{\rho}_{rs}(t)\ , \tag{3.15}$$

which is nothing but the last equality in (3.12).

IV. HAKEN-STROBL PARAMETRIZATION

First, we introduce

$$\gamma_{mn}=\frac{1}{2\hbar^2}\int_{-\infty}^0 d\tau\sum_{\mu,\nu}[(\mathcal{H}_1)_{m\nu,n\mu}(\mathcal{H}_1(\tau))_{n\mu,m\nu}+(\mathcal{H}_1(\tau))_{m\nu,n\mu}(\mathcal{H}_1)_{n\mu,m\nu}]\cdot p_\mu\ . \tag{4.1}$$

Here $\mu,\nu,\ldots$ designate eigenstates of $\mathcal{H}_{\mathrm{ph}}$, i.e., [owing to (3.8)], $p_\mu\delta_{\mu\nu}$ is the initial density matrix of the reservoir (phonons). From (2.6c), we obtain

$$\Xi_{mnrs}\equiv-\frac{1}{\hbar^2}\int_{-\infty}^0 d\tau\,\mathrm{Tr}(A_m[\mathcal{H}_1,[(e^{i\mathcal{L}_0\tau}\mathcal{H}_1),A_r^\dagger\rho_0 A_s]]A_n^\dagger)$$

$$=\frac{1}{\hbar^2}\int_{-\infty}^0 d\tau\sum_{\mu,\nu}\Big[(\mathcal{H}_1)_{m\nu,r\mu}(\mathcal{H}_1(\tau))_{s\mu,n\nu}p_\mu+(\mathcal{H}_1(\tau))_{m\nu,r\mu}(\mathcal{H}_1)_{s\mu,n\nu}p_\mu$$

$$-\delta_{sn}\sum_q(\mathcal{H}_1)_{m\mu,q\nu}(\mathcal{H}_1(\tau))_{q\nu,r\mu}p_\mu-\delta_{rm}\sum_q(\mathcal{H}_1(\tau))_{s\mu,q\nu}(\mathcal{H}_1)_{q\nu,n\mu}p_\mu\Big]\ . \tag{4.2}$$

Thus

$$\Xi_{mmnn}=2\gamma_{mn},\quad m\neq n \tag{4.3}$$

and (neglecting some renormalization and less important terms [8,9])

$$\Xi_{mnmn}\approx-\sum_{a}[\gamma_{am}+\gamma_{an}],\quad m\neq n\ . \tag{4.4}$$

Further, because in general

$$\sum_{m}\Xi_{mmrs}=0\ , \tag{4.5}$$

we have from (4.2),

$$\Xi_{mmmm}=-\sum_{n(\neq m)}2\gamma_{nm}\ . \tag{4.6}$$

Finally, for $m\neq n$, we designate

$$\Xi_{mnnm}\equiv 2\bar{\gamma}_{mn}=\frac{1}{\hbar^2}\int_{-\infty}^{0}d\tau\sum_{\mu,\nu}[(\mathcal{H}_1)_{m\nu,n\mu}(\mathcal{H}_1(\tau))_{m\mu,n\nu}+(\mathcal{H}_1(\tau))_{m\nu,n\mu}(\mathcal{H}_1)_{m\mu,n\nu}]p_\mu\ . \tag{4.7}$$

Neglecting all other [than (4.3), (4.4), (4.6), and (4.7)] coefficients Ξ_{mnrs} and accepting the above notation, we thus have the Haken-Strobl parametrization. This parametrization has originally been suggested for the stochastic Liouville equation model [3,4], but formally, it can also be used here. Notice that for $\lambda=0$, we thus get the Haken-Strobl parametrization in the generalized stochastic Liouville equation model [8,9].

One should first of all realize that this parametrization is not in general exact but becomes so in the limit of diminishing $\mathcal{H}_1$ and generally well includes most of the important terms. Let us now specify the form of γ's introducing (2.6c) into (4.1). It is, still in the second order in $\mathcal{H}_1$,

$$\gamma_{mn}=\frac{1}{2\hbar^2}\int_{-\infty}^{+\infty}d\tau\Big\langle A_m(0)\Big\{\frac{1}{\sqrt{N}}\sum_{qr}\hbar\omega_q(1-\lambda)g_q e^{iqar}A_r^\dagger(\tau)A_r(\tau)[B_q(\tau)+B_{-q}^\dagger(\tau)]+\sum_{r,s}J_{rs}\{\theta_r(\tau)\theta_s^\dagger(\tau)-\langle\theta_r\theta_s^\dagger\rangle\}A_r^\dagger(\tau)A_s(\tau)\Big\}A_m^\dagger(0)\times\Big[\delta_{mn}\frac{1}{\sqrt{N}}\sum_{q'}\hbar\omega_{q'}(1-\lambda)g_{q'}e^{iq'am}(B_{q'}+B_{-q'}^\dagger)+(1-\delta_{mn})J_{mn}\{\theta_m\theta_n^\dagger-\langle\theta_m\theta_n^\dagger\rangle\}\Big]\Big\rangle\ . \tag{4.8}$$

Here $\langle\ \rangle$ means the exciton vacuum average with respect to

$$\exp(-\beta\mathcal{H}_{\rm ph})/\mathrm{Tr}[\exp(-\beta\mathcal{H}_{\rm ph})]\ .$$

Because $\theta_r\theta_s^\dagger-\langle\theta_r\theta_s^\dagger\rangle\sim\lambda$,

$$\gamma_{mn}(\lambda)\to\delta_{mn}\frac{\pi}{N}\sum_{q}|g_q|^2\omega_q^2\frac{1}{N^2}\sum_{k_1}\sum_{k_2}\delta\Big[\omega_q+\frac{1}{\hbar}(J_{k_1}-J_{k_2})\Big][1+2n_B(\hbar\omega_q)]\equiv\delta_{mn}\gamma_{mm}(0),\ n_B(z)=[\exp(\beta z)-1]^{-1}\ , \tag{4.9}$$

when $\lambda\to 0$, while

$$\gamma_{mn}(\lambda)\to(1-\delta_{mn})\frac{1}{N^2}\sum_{k_1,k_2}\sum_{r,s}e^{-ik_1a(r-n)+ik_2a(s-m)}\frac{1}{\hbar^2}J_{rs}J_{mn}\times\tfrac{1}{2}\int_{-\infty}^{+\infty}e^{i(J_{k_1}-J_{k_2})\tau/\hbar}\langle\{\theta_r(\tau)\theta_s^\dagger(\tau)-\langle\theta_r\theta_s^\dagger\rangle\}\{\theta_m\theta_n^\dagger-\langle\theta_m\theta_n^\dagger\rangle\}\rangle d\tau \tag{4.10}$$

for $\lambda\to 1$. Clearly, (4.9) is the Haken-Strobl result, with the diagonal γ_{mm} parameter dominating over the off-diagonal γ's (in our case, owing to our local exciton-phonon interaction, the latter parameters are even exactly zero). Simultaneously, we obtain from (4.9) that still in the second order in $\mathcal{H}_1$, $\gamma_{mm}\to 0$ when $\lambda\to 1$ and $J_{pq}\to 0$. This means that in this order, γ_{mm} is not a parameter given exclusively by the bath. This does not, however, still mean on the other hand that this "disappearance of the site-diagonal dephasing" with diminishing the resonance hopping integral persists even in higher orders in $\mathcal{H}_1$. We shall return to this point later.

Formula (4.10), applicable when $\lambda\to 1$, deserves some further attention. Before doing so, however, let us remember that it means a full disappearance of the local ($m=n$) Haken-Strobl parameter (site local dephasing), in

accordance with GS [1]. In order to proceed in finding a correspondence with the latter work, let us notice that using the Grover- Silbey [1] notation,

$$\gamma_{mn}(\lambda=1)\approx(1-\delta_{mn})\frac{1}{\hbar^2}|\tilde{J}_{mn}|^2\gamma_{nmmn}(+\delta)$$
$$\equiv(1-\delta_{mn})\frac{1}{\hbar^2}|\tilde{J}_{mn}|^2\gamma_1(+\infty) \qquad (4.11)$$

for the nearest neighbors, which is exactly the Grover-Silbey result at long times. The careful reader can recognize that in [1], the γ_1 coefficient depends in general on t. Here we get its infinite-time limit, owing to the Markov approximation used in (3.12). Working as in (3.14) and (3.15), excluding the extention of integrations to infinity, reproduces the result of Grover and Silbey completely. In (4.11), we have only omitted $\tilde{J}_{k_1}$ and $\tilde{J}_{k_2}$ [as small quantities in the exponent under the time integral in (4.10)]. Thus, at $\lambda=1$ (where λ is, as stressed above, still a fully unphysical parameter having no impact on the real regime of the transport as well as its time dependence as far as we are able to avoid approximations), we have the Grover-Silbey result, while at $\lambda=0$, we recover the GSLE [8,9] theory in the Haken-Strobl parametrization. Thus, any formal difference between GSLE [8,9] (or its limit SLE [2,4]) and GS theories [1] is just owing to the above arbitrariness in the choice of λ, i.e., in the choice of representation.

V. CONCLUSIONS

As already stated, we do not see (on grounds of the above arguments) any physical difference between the SLE or GSLE theories on the one hand and the GS-like theories on the other hand. In the above model of the exciton in the periodic chain interacting linearly and locally with harmonic phonons at least, appearance of the local γ_0 parameter, absence of nonlocal γ_1 parameters, and lack of polaron renormalization in the SLE or GSLE approaches is connected with our (possible but ambiguous) choice $\lambda=0$. Thus, it is *not* dictated by physics as usually assumed. This is clearly seen when choosing (again having no arguments provided that we were able to avoid approximations) $\lambda=1$, which then turns our approach (without changing, e.g., the value of the diffusion constant) to the GS [1] one with zero local γ_0 parameter, generally nonzero nonlocal (and J dependent) parameter γ_1, and exciton-resonance (hopping) integral renormalization. (This choice corresponds also to another approach [25], which, however, starts from a different projector and works with just diagonal elements of the dressed-exciton density matrix, i.e., exciton site-occupation probabilities.) Moreover, other (even greater than unity) values of our formal parameter λ (having no impact on, e.g., the regime of transport) are possible and cannot be physically ruled out. The only arguments that might lead to some preference in the choice of λ is that one cannot in fact avoid approximations. Then special values of λ (i.e., picture with or without, e.g., the local parameter γ_0) might become more appropriate than others. This situation must be, however, investigated case by case. To our knowledge, there is still no general criterion for such a choice.

At this point, one should mention that probably the most elaborate and physically deep way of choosing the physically "optimal" value of λ is made by Yarkony and Silbey [26,27]. This method is based on an approximate variational estimate of the *equilibrium* free energy. (It remains an open question whether one could use such an equilibrium optimizing procedure in our situation, which is clearly nonstationary.) As a consequence, λ (though slightly different notation is used in [26,27]) then results in temperature dependence, which yields several interesting phenomena believed to be observed in experiment. One of them is the abrupt extended versus localized transition (exciton localization) of the equilibrium exciton predicted by this approach for sufficiently broad (with respect to the phonon bandwidth) bare-exciton bandwidth with increasing temperature. Transition to such a (self-) localized state (as a time-dependent process) is commonly believed to be observed in, e.g., the delayed exciton luminescence. On the other hand, serious arguments appeared in the last a few years against the possibility of such an abrupt transition [28–39]. The problem, which was not the aim of the present work, deserves further attention. That is why we shall not dwell on this point any longer. One should admit, however, that qualitatively (except that our parameter λ is *fully* free in our approach here) the analytical structure of our formulas corresponds to that of [26,27].

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