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DIFFERENCES AND RECONCILIATION OF THE STOCHASTIC LIOUVILLE EQUATION AND GROVER & SILBEY MODELS

V. Čápek, I. Barvík [1]
Institute of Physics of Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

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An attempt to reconcile two basic kinds of models of the excitation (particle) transfer yielding similar but not identical equations for the single-(quasi)particle density matrix is made. A point in the Grover and Silbey theory connected with necessity to distinguish the bare- and dressed-exciton density matrix is shown which makes a direct comparing with the Stochasic Liouville Equation (SLE) model complicated. Comparison of the SLE model with the original exciton-phonon problem as well as the Generalized Stochastic Liouville Equation (GSLE) model are used to argue that the usual Haken-Strobl-Reineker parameters should not be taken as independent of the exciton transfer integrals J_{mn}. Another alternative of the GSLE model incorporating the small polaron notion is shown to cause the small polaron renormalization of J_{mn} as well as to suppress the diagonal Haken-Strobl parameters γ_{mm}. These changes formally reconcile the GSLE model with the Grover and Silbey theory.

I. INTRODUCTION

In 1971, Grover and Silbey [1] published a microscopic theory of the exciton transfer in molecular crystals which starts from a microscopic Hamiltonian including the Hamiltonians of excitons, phonon bath as well as the exciton-phonon interaction. (As the theory involves no finite-life-time effect, it applies also to migration of charge carriers. The same applies also to other theories discussed below. For simplicity, however, we shall mostly mention just excitons here.) For the simplest case of a fully periodic molecular chain composed of one type of molecules with one molecule per elementary cell, the Hamiltonian of Grover and Silbey can be written as

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{ph} + \mathcal{H}' \tag{1a}$$

with

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

$$\epsilon(k) = \sum_n J_{m-n} e^{-ika(m-n)}, \quad a_k = \frac{1}{\sqrt{N}} \sum_m a_m e^{-ikam} \tag{1b}$$

(notice that here, we use the standard sign convention in the exponent in the Fourier transformation, which is opposite to that in [1]),

$$\mathcal{H}_{ph} = \sum_q \hbar\omega_q b_q^\dagger b_q, \tag{1c}$$

$$\mathcal{H}' = \frac{1}{\sqrt{N}} \sum_{k,q} f(k,q) a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger)$$

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

$$f(k,q) = e^{-iqam} \sum_n \hbar\omega_q g_q^{mn} e^{-ika(m-n)}. \tag{1d}$$

(As compared to the original paper, we assume just one vibrational mode; combination am in exponents designates position of the m-th molecule, i.e. a is the lattice constant and m is integer.) Their theory is based on derivation of equations of motion (differential equations with respect to time) for quantities

$$\mathcal{G}_{nm}(t) = \langle vac_{ex} | A_0 \langle A_n^\dagger(t) A_m(t) \rangle A_0^\dagger | vac_{ex} \rangle \tag{2}$$

which we are going to argue below to correspond to matrix elements $\rho_{mn}(t)$ of the single-exciton density matrix. In (2), $|vac_{ex}\rangle$ is the exciton vacuum state, $\langle | \cdots | \rangle$ designates averaging over phonons in the chain without excitons and, e.g., $A_n^\dagger$ creates a dressed (i.e. small-polaronic) exciton at site n. (Relation of dressed-exciton operators like $A_n^\dagger$ to bare-exciton like $a_n^\dagger$ is given by standard formulae of the canonical transformation theory - see, e.g., (7-8) below.) After some reasonable approximations and omitting unnecessary technical details, these equations of motion read for the nearest neighbour hopping and the local exciton-phonon interaction ($J_{m-n} = J\delta_{m,n\pm1}$)

$$\frac{d}{dt}\mathcal{G}_{nm}(t) = \frac{i}{\hbar}\tilde{J}[\mathcal{G}_{n+1,m}(t) + \mathcal{G}_{n-1,m}(t) - \mathcal{G}_{n,m+1}(t) - \mathcal{G}_{n,m-1}(t)]$$

$$-2\left(\frac{\tilde{J}}{\hbar}\right)^2 \gamma_1(t)[2\mathcal{G}_{nm}(t) - \mathcal{G}_{n+1,m+1}(t)\delta_{nm} - \mathcal{G}_{n-1,m-1}(t)\delta_{nm}$$

$$-\delta_{n,m+1}\mathcal{G}_{mn} - \delta_{n,m-1}\mathcal{G}_{mn}]. \tag{3}$$

Here $\tilde{.}$ designates the corresponding quantity after the small-polaron transformation and $\gamma_1(t)$ describes the influence of the lattice accommodation to a new position of the small-polaronic exciton after its hop in the chain (for introduction see [1]).

There are two basic features of these equations which we should like to discuss here. First, the second (bath-assisted) channel of the excitonic polaron transfer (the

[1] E-mail address: UMFIB@EARN.CVUT.CS

term with the second square bracket on the right hand side of (3)) is proportional to $\tilde{J}^2$, i.e. also to J^2 because [1]

$$\tilde{J}_n = J_n \exp[-N^{-1} \sum_k |X_k^n|^2 (1 - \cos(kan)) \coth(\beta\hbar\omega_k/2)],$$

$$X_k^n = g_k^{nn}. \tag{4}$$

(β is the reciprocal temperature in energy units.)

Second, in (3), there is (in contrast to the theories mentioned below) the same coefficient $2(\tilde{J}/\hbar)^2\gamma_1(t)$ for both $m = n$ and $m \neq n$ in front of the second square bracket in (3). In terms of the Stochastic Liouville Equation (SLE known in a broader sense also as Haken-Strobl) or Generalized Stochastic Liouville Equation (GSLE) models discussed below, the latter characteristic feature can be expressed as a lack of the bath-assisted local energy (i.e. site-diagonal) fluctuation term γ_{mm} usually entering (and often believed to be dominant) the transversal relaxation (damping of the site-off-diagonal elements of the single-exciton density matrix).

These two characteristic features do not correspond to older theories based on the idea that the thermodynamic bath can be well substituted by an external scalar stochastic potential with prescribed statistical properties (usually forming a Gaussian and δ-correlated Markovian process) over which the single-exciton density matrix is then implicitly averaged. This idea goes back to the beginning of sixtieth [2,3] but has been extensively used only after a classical paper by Haken and Strobl [4] (see, e.g., review [5] for many other references) introducing a simple and physically transparent parametrization (the Haken-Strobl parametrization or the Haken-Strobl-Reineker model). In spite of differences this two descriptions had been long time taken as formally identical [5, 19, 20]. Without necessary invoking this parametrization, the approach is also often called the Stochastic Liouville Equation model. In the above parametrization scheme, the resulting equations of motion for the exciton density matrix read in our model

$$\frac{d}{dt}\rho_{mn}(t) = -\frac{i}{\hbar}([H_{ex}, \rho(t)])_{mn}$$
$$+2\delta_{mn} \sum_p \gamma_{mp}[\rho_{pp}(t) - \rho_{mm}(t)]$$
$$-(1 - \delta_{mn})[2\Gamma\rho_{mn}(t) - 2\bar{\gamma}_{mn}\rho_{nm}(t)] \tag{5a}$$

with

$$\Gamma = \sum_p \gamma_{pm} = \gamma_{mm} + \sum_{p(\neq m)} \gamma_{pm}. \tag{5b}$$

(In fact, because of the periodicity of the problem, all γ_{mn} depend just on the relative position $m - n$; we do not, however, write γ_{m-n} instead so as to avoid possible confusion with, e.g., the Grover and Silbey parameter $\gamma_1(t)$ - see above.) Provided that one neglects all J_{m-n} and γ_{mn} for $|m-n| > 1$, (5) acquires the same structure as (3) provided that

- one can identify

$$J \equiv J_1 \approx \tilde{J}, \tag{6a}$$

$$\gamma_{m,m\pm1} \approx \bar{\gamma}_{m,m\pm1} \approx (\frac{\tilde{J}}{\hbar})^2\gamma_1(t), \tag{6b}$$

- and set $\gamma_{mm} \approx 0$.

In (6b), the identification of $\gamma_{m,m\pm1}$ with $\bar{\gamma}_{m,m\pm1}$ is compatible with approximations used in [1] (compare the text below Eq. (33) of the Grover and Silbey's work). Also (6a) could be explained realizing that because of substitution of the real phonon bath by the stochastic field, the Stochastic Liouville Equation model cannot describe the polaron effects (which, on the other hand, could be sufficiently small in some specific situations). The necessity to neglect the coefficient γ_{mm} (currently assumed and argued to be dominating over all other γ_{mn}, $m \neq n$) and proportionality of $\gamma_{m,m\pm1}$ (steming in the usual formulation just from the potential field) to J^2 is, however, a relevant problem which has already been mentioned above and which is the motivation of the present paper. One should add here that inspite of (6a-b) as well as tiny technical differences in the derivation, the Grover and Silbey theory [1] is currently understood to be physically equivalent to SLE [5–7].

Partial explanation could be given by the observation that the Grover and Silbey theory [1] is based on the local *linear* (in the phonon creation and annihilation operators $b^\dagger$ and b) exciton-phonon interaction Hamiltonian $\mathcal{H}'$. Adding, e.g., a quadratic term should add (to (1)) a term corresponding to γ_{mm} in the Stochastic Liouville Equation model. We do not believe, however, that this is the genuine explanation. The point is that using the same Hamiltonian (1a-d) as Grover and Silbey [1] (i.e. with just the linear exciton-phonon coupling), one can fully keep the quantum character of the phonon bath but follow otherwise the way of reasoning which is typical of the Stochastic Liouville Equation model. This approach first published in [8] is sometimes called the Generalized Stochastic Liouville Equation model. For non-periodic systems, it provides a generalization of the Stochastic Liouville Equation model (corresponding rather to infinite temperature) to finite temperatures. In the Haken-Strobl parametrization and in our model, it, however, fully reproduces Eqs. (5) **including** the crucial (diagonal) parameter γ_{mm} (see below). So, to our opinion, the problem is more complicated and we hope to submit at least a contribution to its solution here.

II. CONNECTION BETWEEN DENSITY MATRIX AND GROVER & SILBEY PARAMETERS

In this Section, we first give arguments why the Grover and Silbey's parameters $\mathcal{G}_{nm}(t)$ as introduced in (2) are currently [5–7] but incorrectly (as shown then below) understood to coincide with matrix elements $\rho_{mn}(t)$ of the single-exciton density matrix for our problem of the exciton initially created in the exciton-free chain with phonons in thermal equilibrium. This would then require the coincidence of equations (3) of the Grover and Silbey theory with (5) of the SLE (or GSLE) theory.

As already mentioned in the Introduction, Grover and Silbey [1] work with small polaron (clothed exciton) quantities, i.e. apply first the small polaron (canonical) transformation to relevant physical operators. So, e.g., the new electron annihilation and phonon annihilation time-independent operators read (again, notice the difference in the sign convention)

$$A_n = e^{-S} a_n e^{S},$$

$$B_k = e^{-S} b_k e^{S} \tag{7}$$

with

$$S = N^{-1/2} \sum_{nk} X_k^{-n} a_n^\dagger a_n (b_k^\dagger - b_{-k}). \tag{8}$$

Now, we could rewrite the Grover and Silbey definition (2) as

$$\mathcal{G}_{nm}(t) = \langle A_n^\dagger(t) A_m(t) \rangle \tag{9}$$

where the averaging, using standard formulae of the theory of canonical transformations,

$$\langle \cdots \rangle = \mathrm{Tr}(\rho_{pol} \cdots),$$

$$\rho_{pol} = A_0^\dagger |vac_{ex}\rangle\langle vac_{ex}| A_0 \otimes \frac{e^{-\beta \sum_k \hbar\omega_k B_k^\dagger B_k}}{\mathrm{Tr}_{ph}\, e^{-\beta \sum_k \hbar\omega_k B_k^\dagger B_k}}$$

$$= e^{-S} a_0^\dagger |vac_{ex}\rangle\langle vac_{ex}| a_0 \otimes \frac{e^{-\beta \sum_k \hbar\omega_k b_k^\dagger b_k}}{\mathrm{Tr}_{ph}\, e^{-\beta \sum_k \hbar\omega_k b_k^\dagger b_k}} e^{S} \equiv e^{-S} \rho(0) e^{S}. \tag{10}$$

Clearly, $\rho(0)$ is the initial density matrix of the system corresponding to the situation that one exciton is created at time $t = 0$ in the otherwise excitonless chain with a thermal distribution of the phonons. Consequently,

$$\mathcal{G}_{nm}(t) = \mathrm{Tr}(e^{-S}\rho(0)e^{S} e^{-S} e^{\frac{i}{\hbar}\mathcal{H}t} a_n^\dagger e^{-\frac{i}{\hbar}\mathcal{H}t} e^{S}$$

$$\cdot e^{-S} e^{\frac{i}{\hbar}\mathcal{H}t} a_m e^{-\frac{i}{\hbar}\mathcal{H}t} e^{S}) = \mathrm{Tr}(e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(0) e^{\frac{i}{\hbar}\mathcal{H}t} a_n^\dagger a_m)$$

$$= \mathrm{Tr}(\rho(t) a_n^\dagger a_m) \equiv \rho_{mn}(t). \tag{11}$$

This formally makes our proof of the usual (see e.g. [6,7]) but incorrect (as we are going to show below) assertion that Grover and Silbey's quantities $\mathcal{H}_{nm}(t)$ correspond to the usual matrix elements of the single-exciton density matrix complete.

A word of caution is, however, necessary here. In the above proof, we have assumed that the proper definition of the meaning of, e.g., the Grover and Silbey's symbol $A_m(t)$ (the dressed-exciton annihilation operator at site m in the Heisenberg representation) is

$$A_m(t) = e^{-S} e^{\frac{i}{\hbar}\mathcal{H}t} a_m e^{-\frac{i}{\hbar}\mathcal{H}t} e^{S}$$

$$= e^{\frac{i}{\hbar}\tilde{\mathcal{H}}t} A_m e^{-\frac{i}{\hbar}\tilde{\mathcal{H}}t} \tag{12a}$$

with

$$\tilde{\mathcal{H}} = e^{-S}\mathcal{H}e^{S} = \tilde{\mathcal{H}}_{ex} + \tilde{\mathcal{H}}_{ph} + \tilde{\mathcal{H}}' \tag{12b}$$

$$\tilde{\mathcal{H}}_{ex} = \sum_{m \neq n} J_{m-n} A_m^\dagger A_n,$$

$$\tilde{\mathcal{H}}_{ph} = \sum_q \hbar\omega_q B_q^\dagger B_q,$$

$$\tilde{\mathcal{H}}' = \frac{1}{\sqrt{N}} \sum_{mn} g_q^{mn} \hbar\omega_q A_m^\dagger A_n. \tag{12c}$$

This and only this is, to our opinion, the proper form which is compatible with the usual Schrödinger form of the quantum mechanics as far as one really assumes that the canonical transformation has been made. On the other hand, from, e.g., Eq. (20) of [1], it can be seen that Grover and Silbey used (instead of (12a-b)) the definition

$$A_m(t) = e^{\frac{i}{\hbar}\mathcal{H}t} A_m e^{-\frac{i}{\hbar}\mathcal{H}t}. \tag{13}$$

(The same point can be found in a previous work of the same authors [9].) This would be, to our opinion, generally incorrect in the canonical transformation context and in this case, it could really serve as the first reason why one should be careful when comparing results of the Grover and Silbey's [1] with those of other theories. On the other hand, this only means that Grover and Silbey do not in fact use the canonical transformation. They simply put questions which are *by the definition* connected with excitonic polarons. For this reason, they introduce and work with the dressed-exciton (small excitonic polaron) creation and annihilation operators $A_n^\dagger$ and A_n known from the canonical transformation theory, but their wave functions and other operators like the Hamiltonian are untransformed with $\mathcal{H}$ being only rewritten in terms of the dressed-exciton operators. Thus, for the same Hamiltonian $\mathcal{H}$ as in (1a),

$$\mathcal{H} = \mathcal{H}_{pol} + \tilde{\mathcal{H}}_{ph} + \mathcal{H}_{int}, \tag{1e}$$

$$\mathcal{H}_{pol} = \sum_k \tilde{\epsilon}(k) A_k^\dagger A_k,$$

$$\tilde{\epsilon}(k) = -\frac{1}{N}\sum_q |X_q^n|^2 \hbar\omega_q + \sum_n e^{ikan} J_n \langle \Theta_{n+m}^\dagger \Theta_m \rangle, \tag{1f}$$

$$\mathcal{H}_{int} = \frac{1}{N} \sum_{n \neq m, k, k'} e^{ia(kn-k'm)} J_{n-m} (\Theta_n{}^\dagger \Theta_m - \langle \Theta_n^\dagger \Theta_m \rangle) A_k^\dagger A_{k'} \equiv \sum_{kk'} V_{kk'} A_k^\dagger A_{k'},$$

$$\Theta_n = \exp[-N^{-1/2} \sum_k X_k^{-n} (B_k^\dagger - B_{-k})]. \tag{1g}$$

(Here, we set $g_q^{mn} = 0, m \neq n$ in accordance with [1]; for $\tilde{\mathcal{H}}_{ph}$ see (12c) above.) So, in particular and instead of (9-10),

$$\mathcal{G}_{nm}(t) = \mathrm{Tr}(\rho(0) A_n^\dagger(t) A_m(t))$$

$$= \mathrm{Tr}(\rho(t) A_n^\dagger A_m)$$

$$= \mathrm{Tr}(\rho(t) e^{-S} a_n^\dagger a_m e^{S})$$

$$= \mathrm{Tr}(\rho(t)\{a_n^\dagger a_m + [a_n^\dagger a_m, S] + \frac{1}{2}[[a_n^\dagger a_m, S], S] + \cdots\}) \qquad (14)$$

with

$$\rho(t) = \mathrm{e}^{\frac{i}{\hbar}\mathcal{H}t}\rho(0)\mathrm{e}^{-\frac{i}{\hbar}\mathcal{H}t},$$

$$\rho(0) = A_0^\dagger \rho_0 A_0. \qquad (15)$$

Here ρ_0 is the initial density matrix of the chain (including phonons) without excitons. From (14), one easily finds that $\mathcal{G}_{nn}(t) = \rho_{nn}(t) = P_n(t)$ really gives the probability of finding the (bare as well as dressed) exciton at site n. On the other hand, the off-diagonal elements of $\mathcal{G}_{nm}(t)$ given by (14) and of the bare-exciton density matrix $\rho_{mn}(t)$ never in general coincide. Thus, contrary to (11), $\mathcal{G}_{nm}(t)$ given by (14) does *not* (irrespective of the similarities of (3) and (5) as well as coincidence of the site-diagonal elements) represent the mn-element of the bare-exciton but rather that of the dressed-exciton (or exciton-polaron) density matrix.

III. SLE FROM THE POINT OF VIEW OF GSLE THEORY.

Here, we want to argue first of all that irrespective of the above misinterpretation of basic quantities of the Grover and Silbey theory [5,6,7], not all the discrepancies between (3) and (5) can be ascribed to it. Traditionally, as in [6], one could start here from the time-convolution Generalized Master Equations (TC-GME) based on the Nakajima and Zwanzig identity [10-12]

$$\frac{\partial}{\partial t}D\tilde{\rho}(t) = -iD\tilde{\mathcal{L}}_1(t)D\tilde{\rho}(t)$$

$$-\int_{t_0}^{t} D\tilde{\mathcal{L}}_1(t)\exp_{\leftarrow}[-i(1-D)\int_{\tau}^{t}\tilde{\mathcal{L}}_1(\tau)\,\mathrm{d}\tau](1-\mathrm{D})\tilde{\mathcal{L}}_1(\tau)\mathrm{D}\tilde{\rho}(\tau)\,\mathrm{d}\tau$$

$$-iD\tilde{\mathcal{L}}_1(t)\exp_{\leftarrow}[-i\int_{t_0}^{t}(1-D)\tilde{\mathcal{L}}_1(\tau)\,\mathrm{d}\tau](1-\mathrm{D})\tilde{\rho}(\mathrm{t}_0). \qquad (16)$$

Equivalent from the physical point of view but a bit simpler way is to work with the time-convolutionless Generalized Master Equations (TCL-GME) based on, e.g., the Shibata, Hashitsume, Takahashi and Shingu identity [13,14]

$$\frac{\partial}{\partial t}D\tilde{\rho}(t) = -iD\tilde{\mathcal{L}}_1(t)[1 + i\int_{t_0}^{t}\mathcal{G}(t,\tau)(1-D)\tilde{\mathcal{L}}_1(\tau)DG(t,\tau)\,\mathrm{d}\tau]^{-1}$$

$$\cdot[D\tilde{\rho}(t) + \mathcal{G}(t,t_0)(1-D)\tilde{\rho}(t_0)]. \qquad (17)$$

Here $\tilde{\cdots}$ designates the interaction picture, i.e.

$$\tilde{\rho}(t) = \mathrm{e}^{\frac{i}{\hbar}\mathcal{H}_0(t-t_0)}\rho\mathrm{e}^{-\frac{i}{\hbar}\mathcal{H}_0(t-t_0)} = \mathrm{e}^{i\mathcal{L}_0(t-t_0)}\rho(t), \qquad (18a)$$

$$\mathcal{L}_1(t) = \mathrm{e}^{i\mathcal{L}_0(t-t_0)}\mathcal{L}_1\mathrm{e}^{-i\mathcal{L}_0(t-t_0)}, \qquad (18b)$$

$$\mathcal{L}_0 = \frac{1}{\hbar}[\mathcal{H}_0, \cdots], \qquad (18c)$$

and

$$\mathcal{L}_1 = \frac{1}{\hbar}[\mathcal{H}_1, \cdots] \qquad (18d)$$

where

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \qquad (19)$$

is so far arbitrary way of splitting our Hamiltonian $\mathcal{H}$ in (1) into a "perturbed" and "unperturbed" part. Finally,

$$G(t,\tau) = \exp_{\rightarrow}[i\int_{\tau}^{t}\tilde{\mathcal{L}}_1(s)\,\mathrm{d}s] \qquad (20a)$$

and

$$\mathcal{G}(t,\tau) = \exp_{\leftarrow}[-i\int_{\tau}^{t}(1-D)\tilde{\mathcal{L}}_1(s)\,\mathrm{d}s]. \qquad (20b)$$

In what follows, we partly proceed as in [15].

Finally, let us specify our projector $D(= D^2)$. We use the Argyres and Kelley form [16]

$$DA = (\mathrm{Tr}_R A)\otimes\varrho^R, \qquad \mathrm{Tr}_R\varrho^R = 1 \qquad (21)$$

where ϱ^R is otherwise so far undetermined operator in the Hilbert space of the reservoir (phonons); $\mathrm{Tr}_R\cdots$ designates the trace in this Hilbert space only. Then

$$\frac{\partial}{\partial t}D\tilde{\rho}(t) = D\frac{\partial}{\partial t}\left(\mathrm{e}^{i\mathcal{L}_0(t-t_0)}\rho(t)\right)$$

$$= \mathrm{e}^{i\mathcal{L}_{ex}(t-t_0)}[i\mathcal{L}_{ex} + \frac{\partial}{\partial t}]D\rho(t). \qquad (22)$$

Here, we have introduced $\mathcal{L}_{ex}$ as

$$D\mathcal{L}_0 = \mathcal{L}_{ex}D. \qquad (23)$$

For the initial condition, we will always assume that initially, the total exciton-reservoir (phonon) density matrix is separable

$$\rho(t_0) = \rho_S(t_0)\otimes\rho_R(t_0),$$

$$\rho_S(t) \equiv \rho_{ex}(t) = \mathrm{Tr}_R\rho(t), \qquad \rho_R(t) \equiv \rho_{ph}(t) = \mathrm{Tr}_S\rho(t). \qquad (24)$$

Here, $\mathrm{Tr}_S\cdots$ designates the trace in the Hilbert space of the system (exciton) only. As we assume only one exciton in the system, ρ_{ex} is simultaneously the single-(bare-)exciton density matrix. Then, taking in (21)

$$\varrho^R = \rho_R(t_0), \qquad (25)$$

$$(1-D)\tilde{\rho}(t_0) = (1-D)\rho(t_0) = 0 \qquad (26)$$

and (16) as well as (17) become more simple.

Now, let us make (19) more specific choosing

$$\mathcal{H}_0 = \mathcal{H}_{ex} + \mathcal{H}_{ph},$$

$$\mathcal{H}_1 = \mathcal{H}'. \tag{27}$$

Then (23) applies with

$$\mathcal{L}_{ex} = \frac{i}{\hbar}[\mathcal{H}_{ex}, \cdots] \tag{28}$$

and in terms localized single-exciton states $|m\rangle = a_m^\dagger |vac_{ex}\rangle$, Eq. (17) reads after taking Tr_R

$$\frac{\partial}{\partial t}\rho_{mn}(t) = -\frac{i}{\hbar}[\mathcal{H}_{ex}, \rho(t)]_{mn} + \sum_{pq} \Xi_{mnpq}(t, t_0)\rho_{pq}(t), \tag{29}$$

$$\Xi_{mnpq}(t, t_0) = -i\sum_{\mu\nu\lambda}[e^{-i\mathcal{L}_0(t-t_0)}D\tilde{\mathcal{L}}_1(t)[1 + i\int_{t_0}^{t} \mathcal{G}(t,\tau)(1-D)\tilde{\mathcal{L}}_1(\tau)DG(t,\tau)]^{-1}$$

$$\cdot De^{i\mathcal{L}_0(t-t_0)}]_{m\mu,n\mu,p\nu,q\lambda}\varrho_{\nu\lambda}^R$$

$$\approx \sum_{\mu\nu\lambda}[\mathcal{L}_1(1-D)\int_{t_0-t}^{0} ds\tilde{\mathcal{L}}_1(s)]_{m\mu,n\mu,p\nu,q\lambda}\varrho_{\nu\lambda}^R + \mathcal{O}(\mathcal{L}_1^3). \tag{30}$$

Here the indices $m\mu$, $n\nu$ etc. are related to the exciton-phonon states

$$|m\mu\rangle \equiv |m\{\mu_k\}\rangle = a_m^\dagger \prod_k (\frac{1}{\sqrt{\mu_k!}}(b_k^\dagger)^{\mu_k})|vac_{ex-ph}\rangle. \tag{31}$$

Now, Eq. (29) determine what is called the Generalized Stochastic Liouville Equation (GSLE) model as the structure of (29) is the same as in the usual Stochastic Liouville Equation approach except for some lacking symmetries [13]. Usually, as we shall also do henceforth, one neglects the time-dependence of $\Xi_{mnpq}(t, t_0)$. This may become well justified provided that the dynamics of the bath is much faster than that of the system (which is, by the way, one of the basic assumptions of the standard Stochastic Liouville Equation model [5]). Starting from (14) as in [8], the same physical assumption would justify the Markov approximation yielding then the same set of equations.

In the Haken-Strobl [4] parametrization, we set (see [8] or [15])

$$\Xi_{mmmm} = -\sum_{n(\neq m)} \Xi_{nnmm}, \tag{32a}$$

$$\Xi_{mmnn} = 2\gamma_{mn},\ m \neq n, \tag{32b}$$

$$\Xi_{mnmn} \approx -\sum_r(\gamma_{rm} + \gamma_{rn}),\ m \neq n, \tag{32c}$$

$$\Xi_{mnnm} \equiv 2\bar{\gamma}_{mn},\ m \neq n \tag{32d}$$

and neglect all other Ξ's. (Here (32d) and (32b) serve as a definition of $\bar{\gamma}_{mn}$ and γ_{mn} for $m \neq n$ while (32c) may serve as a definition of γ_{mm}). Invoking the symmetry of our model (periodic monomolecular chain), one rederives (5a-b).

Now, we can start our discussion of the SLE model from the point of view of the GSLE approach. In order to make a hint from the very beginning, let us mention

that in the SLE model, the stochastic potential field substituting the phonons may be, except for the above limitations (Gaussian and δ-correlated Markov character), more or less arbitrary. This makes the Haken-Strobl parameters γ_{mn} and $\bar{\gamma}_{mn}$ (except for their definiteness and some symmetry relations) practically arbitrary in the SLE model. However, here we want to argue that, in order to keep a connection with the original notion of the reservoir (i.e. with the GSLE model preserving it on every stage), these limitations are not sufficient.

Having that goal in mind let us mention that in the SLE model (Eqs. (2.13) and (2.12) of [5])

$$\gamma_{mn} \equiv \gamma_{mn}^{SLE} = \Lambda(m,n,m,n) = \frac{1}{2}\int \langle h_{mn}(0)h_{nm}(t)\rangle\, dt$$

$$= \frac{1}{2}\langle h_{mn}(0)h_{nm}^{\omega=0}\rangle. \tag{33}$$

Here $\langle\cdots\rangle$ designates the statistical averaging over the above stochastic field while $h_{mn}(t)$ are matrix elements of this field between two localized states of the exciton. h_{mn}^{ω} is then the corresponding Fourier component. So, in order to keep the correspondence with the original microscopic Hamiltonian (1), one should take as counterparts

$$\sum_{mn} h_{nm}(t)a_n^\dagger a_m \sim e^{\frac{i}{\hbar}\mathcal{H}_0(t-t_0)}\mathcal{H}_1 e^{-\frac{i}{\hbar}\mathcal{H}_0(t-t_0)}$$

$$= \sum_{mn} a_n^\dagger a_m \sum_q \sum_{n'm'} \frac{1}{\sqrt{N}} g_q^{n'm'} \hbar\omega_q \frac{1}{N^2}\sum_{k_1k_2} e^{-ik_1a(n'-n)+ik_2a(m'-m)} e^{\frac{i}{\hbar}(J(k_1)-J(k_2))t}$$

$$\cdot[b_q e^{-i\omega_q t} + b_q^\dagger e^{i\omega_q t}]. \tag{34}$$

Here we use the property that $\omega_q = \omega_{-q}$ and introduce $J(k) = \sum_n J_{mn}\exp(-ika(m-n))$. So, extracting $h_{nm}(t)$, we get

$$h_{nm}^{\omega} \sim \frac{1}{\sqrt{N}}\sum_{n'm'}\sum_q g_q^{n'm'}\hbar\omega_q \frac{1}{N^2}\sum_{k_1k_2} e^{-ik_1a(n'-n)+ik_2a(m'-m)}$$

$$\cdot[b_q \cdot 2\pi\delta(\omega - \omega_q + (J(k_1) - J(k_2))/\hbar) + b_{-q}^\dagger \cdot 2\pi\delta(\omega + \omega_q + (J(k_1) - J(k_2))/\hbar)]. \tag{35}$$

Consequently, for $J_{mn} = 0$, $h_{nm}^{\omega=0}$ should be taken as zero, i.e. $\gamma_{mn} \to 0$ when $J_{mn} \to 0$ as a consequence of the fact that $g_{q=0}^{nm} = 0$ (there is no interaction of the exciton with a homogeneous shift of the crystal). This well corresponds to (but does not imply) the proportionality of γ's to J^2 mentioned in the introduction.

Now, let us return to the central point here, i.e. how the dependence of the Haken-Strobl parameters γ_{mn} on J_{mn} follows from the analogy between the SLE and GSLE models. If we really do identify the γ-parameters from these two approaches, we can start from (32b-c). In the lowest order in the exciton-phonon coupling (compatible with the area of applicability of the standard SLE), we get for both $m \neq n$ and $m = n$ [13]

$$\gamma_{mn} \equiv \gamma_{mn}^{GSLE} \approx \frac{\pi\hbar}{N}\sum_q \omega_q^2 |g_q^{mn}|^2$$

$$\cdot[\delta(\varepsilon_m - \varepsilon_n + \hbar\omega_q)[n_B(\hbar\omega_q) + 1] + \delta(\varepsilon_m - \varepsilon_n - \hbar\omega_q) n_B(\hbar\omega_q)] \tag{36}$$

provided that one can set all J_{mn} zero. For general case see (39) below. In (36), $n_B(z) = [\exp(\beta z)-1)^{-1}$ is the Bose-Einstein distribution function and ε_m designate the local exciton energies in the lattice. In our periodic chain, all these ε_m are equal (we have already set them zero in our starting Hamiltonian(1)). Thus, from (36), we get

$$\gamma_{mn} \to 0, \qquad J_{mn} \to 0, \tag{37}$$

while for $J_{mn} \neq 0$, γ_{mn} result in general nonzero [13]. This corresponds to the Grover and Silbey result [1]. At the end, let us just mention that in the GSLE (and, similarly, SLE) model, we (on the contrary) observe no direct correspondence of γ_{mn} and $\tilde{\gamma}_{nm}$ as in the Grover and Silbey equations (3).

IV. PROBLEM OF THE SITE-DIAGONAL HAKEN-STROBL PARAMETER.

In the Introduction, we have mentioned also another feature which seems to distinguish between the Grover & Silbey and SLE models appreciably. The point is that in the usual SLE as well as the version of the GSLE model discussed in the last Section, there is in general nonzero site-diagonal element γ_{mm} which is on the other hand fully lacking in the Grover and Silbey theory [1] (compare (3)). We have already mentioned that, to our opinion and in contrast with a standard explanation, this is not owing to the linear (in the lattice-point displacements) exciton-phonon coupling Hamiltonian $\mathcal{H}'$ of the Grover and Silbey theory. The reason is that for the same Hamiltonian, GSLE (see [8,15] or the previous Section) yields γ_{mm} nonzero.

Before presenting our explanation of this interesting observation, let us mention that the presence of the positive site-diagonal γ_{mm}'s in the SLE seems to correspond to the usual (and often uncritically accepted) inequality between the longitudinal and transversal relaxation times T_1 and T_2

$$T_1 \geq 0.5\,T_2. \tag{38}$$

The reason is that γ_{mm} (which are always non-negative) contribute to the damping of the off-diagonal elements ρ_{mn} but do not directly influence the time development of the diagonal elements in (5a). Really, in the Haken-Strobl [4] parametrization of SLE and with zero exciton transfer integral, (38) is well fulfilled but turns to equality upon setting γ_{mm} zero. In words, one can interpret (38) by saying that each act of the longitudinal relaxation (hop) automatically destroys the phase coherence. One can arrive at (38) also realizing that there are in general mechanisms (types of the exciton-phonon coupling in our situation) which yield no longitudinal but nonzero transversal relaxation. (It should be, however, always kept in mind whether one speaks about the longitudinal and transversal relaxation in terms of the *bare-* or *dressed*-exciton density matrix.)

Relation (38) is often believed to be universal; at least on the level of the lowest order perturbation theory, the arguments leading to (38) seem to be undoubted.

On the other hand, one should mention that, e.g., the GSLE is by no means in general the lowest order theory. Skinner, Reineker et al [17-19] have recently proved that under specific conditions (lying, however, beyond the range of undoubted applicability of the standard SLE model), relation (38) might become violated. So, one should ask (having in mind the lack of the corresponding term in the Grover and Silbey theory) whether the presence of γ_{mm}'s in the GSLE as above is a matter of necessity or if it is owing to, e.g., some arbitrariness involved.

Our answer to the second alternative is confirmative. In order to show that, let us first of all quote the lowest order result (in $\mathcal{H}_1$ but exact to the infinite order in all other parameters included in $\mathcal{H}_0$ possibly like J_{mn})

$$\gamma_{mm} \approx \frac{1}{2\hbar^2}\int_{-\infty}^{0} ds \sum_{\mu\nu}[(\mathcal{H}_1)_{m\mu,m\nu}(\tilde{\mathcal{H}}_1)_{m\nu,m\mu}(s) + (\mathcal{H}_1)_{m\nu,m\mu}(\tilde{\mathcal{H}}_1)_{m\mu,m\nu}(s)]p_\nu. \tag{39}$$

(see [8,15]). Here, for simplicity, we have taken $\varrho^R_{\mu\nu} = \delta_{\mu\nu}p_\nu$. Assume now that instead of (27) we choose

$$\mathcal{H}_0 = \mathcal{H}_{ex} + \mathcal{H}_{ph}$$
$$+\frac{1}{\sqrt{N}}\sum_m\sum_q g_q^{mm}\hbar\omega_q(b_q + b^\dagger_{-q}),$$
$$\mathcal{H}_1 = \frac{1}{\sqrt{N}}\sum_{m\neq n}\sum_q g_q^{mn}\hbar\omega_q(b_q + b^\dagger_{-q}). \tag{40}$$

Then, from the very difinition of $\mathcal{H}_1$, we find that

$$\gamma_{mm} \approx 0, \tag{41}$$

but

$$\gamma_{mn} \neq 0 \tag{42}$$

in (39). This disagrees with the standard SLE as well as the version of the GSLE mentioned in the previous Section. On the other hand, it formally fully corresponds to the Grover and Silbey [1] result (3). Detailed inspection shows, however, that our choice (40) does not in fact solve the problem of the correspondence with the Grover and Silbey theory. The point is that in this way, we never obtain corresponding results for quantity $\gamma_1(t)$ entering (3) and, in particular, the proportionality (6b) above (as $\mathcal{H}_1$ from (40) is fully neglected in [1]). In order to achieve that, we have to resort to a new form of projector

$$D\cdots = \sum_{k_1k_2}\mathrm{Tr}(A_{k_1}\cdots A^\dagger_{k_2})A^\dagger_{k_1}\rho_0 A_{k_2}$$
$$= \sum_{mn}\mathrm{Tr}(A_m\cdots A^\dagger_n)A^\dagger_m\rho_0 A_n,$$
$$\rho_0 = |vac_{ex}\rangle\langle vac_{ex}| \otimes \frac{e^{-\beta\mathcal{H}_{ph}}}{\mathrm{Tr}_{ph}e^{-\beta\mathcal{H}_{ph}}}. \tag{43}$$

Clearly, $D\rho(t)$ is then a linear combination of independent operators $A_m^\dagger \rho_0 A_n$ with coefficients $\mathcal{G}_{nm}(t) = \mathrm{Tr}(\rho(t)A_n^\dagger A_m)$ (see (14)) which are nothing but the mn-elements of the (single-particle) dressed exciton density matrix. In particular, in (14), we choose

$$\mathcal{H}_0 = \mathcal{H}_{pol} + \tilde{\mathcal{H}}_{ph},$$
$$\mathcal{H}_1 = \mathcal{H}_{int} \propto J \tag{44}$$

(see (1e-g) above). Here, in correspondence with [1], we set $g_q^{mn} = 0$, $m \neq n$. Then

$$\sum_{mn} A_m^\dagger \rho_0 A_n \frac{\partial}{\partial t}\mathcal{G}_{nm}(t) \equiv \sum_{mn} A_m^\dagger \rho_0 A_n \frac{\partial}{\partial t}\mathrm{Tr}(A_m \rho(t) A_n^\dagger)$$
$$= \sum_{mn} A_m^\dagger \rho_0 A_n \mathrm{Tr}(A_m e^{iL_{pol}\cdot(t-t_0)}[-iL_{pol}\tilde{\rho}(t) + \frac{\partial}{\partial t}\tilde{\rho}(t)]A_n^\dagger)$$
$$= \sum_{mn} A_m^\dagger \rho_0 A_n \{-\frac{i}{\hbar}\mathrm{Tr}(A_m[\mathcal{H}'_{pol}, \rho(t)]A_n^\dagger)$$
$$+\mathrm{Tr}(a_m e^{-\frac{i}{\hbar}\mathcal{H}'_{pol}\cdot(t-t_0)} e^S \frac{\partial\tilde{\rho}}{\partial t} e^{-S} e^{\frac{i}{\hbar}\mathcal{H}'_{pol}\cdot(t-t_0)} a_n^\dagger)\}. \tag{45}$$

Here, as compared to (1f) and (1b),

$$\mathcal{H}'_{pol} = \sum_k \tilde{\epsilon}(k) a_k^\dagger a_k \tag{46}$$

is the renormalized (i.e. including the polaron shifts and renormalization of J - see (4)) free bare exciton Hamiltonian. Thus

$$\sum_{mn} A_m^\dagger \rho_0 A_n \frac{\partial}{\partial t}\mathcal{G}_{nm}(t)$$
$$= \sum_{mn} A_m^\dagger \rho_0 A_n \{-\frac{i}{\hbar}\mathrm{Tr}(A_m[\mathcal{H}'_{pol}, \rho(t)]A_n^\dagger)$$
$$+\sum_{rs}\langle m|e^{-\frac{i}{\hbar}\mathcal{H}'_{pol}\cdot(t-t_0)}|r\rangle\langle s|e^{\frac{i}{\hbar}\mathcal{H}'_{pol}\cdot(t-t_0)}|n\rangle\,\mathrm{Tr}(A_r \frac{\partial\tilde{\rho}}{\partial t} A_s^\dagger)\}$$
$$= \sum_{mn} A_m^\dagger \rho_0 A_n \{-\frac{i}{\hbar}\mathrm{Tr}(A_m[\mathcal{H}'_{pol}, \rho(t)]A_n^\dagger) + \sum_{rs}(e^{-iL'_{pol}\cdot(t-t_0)})_{mnrs}\,\mathrm{Tr}(A_r \frac{\partial\tilde{\rho}}{\partial t} A_s^\dagger)\}. \tag{47}$$

Here, $|m\rangle = a_m^\dagger|vac_{ex}\rangle$ etc. and $L'_{pol}\cdots = \frac{1}{\hbar}[\mathcal{H}'_{pol}, \cdots]$. Term $\mathrm{Tr}(A_r \frac{\partial\tilde{\rho}}{\partial t} A_s^\dagger)$ on the right hand side can be deduced from (17). Assuming that the initial condition term disappears (which follows in our case from (43) when $\rho(0) = A_0^\dagger \rho_0 A_0$) we obtain

$$\mathrm{Tr}(A_r \frac{\partial\tilde{\rho}}{\partial t} A_s^\dagger)$$
$$= -i\mathrm{Tr}(A_r(\tilde{\mathcal{L}}_1(t)[1 + i\int_{t_0}^t \mathcal{G}(t,\tau)(1-D)\tilde{\mathcal{L}}_1(\tau)DG(t,\tau)\,d\tau]^{-1}D\tilde{\rho}(t))A_s^\dagger)$$

$$\approx -\sum_{pq}\mathrm{Tr}(A_r(\tilde{\mathcal{L}}_1(t)\int_{t_0}^t(1-D)\tilde{\mathcal{L}}_1(\tau)\,d\tau\, A_p^\dagger \rho_0 A_q)A_s^\dagger)\cdot\mathrm{Tr}(A_p\tilde{\rho}A_q^\dagger). \tag{48}$$

Thus, combining (47) and (48), we obtain

$$\frac{\partial}{\partial t}\mathcal{G}_{nm}(t) = -\frac{i}{\hbar}([\mathcal{H}'_{pol}, \rho(t)])_{mn}$$
$$-\sum_{pq}\mathrm{Tr}(A_m(\mathcal{L}_1 e^{-iL'_{pol}\cdot(t-t_0)}\int_{t_0}^t(1-D)\tilde{\mathcal{L}}_1(\tau)\,d\tau\, A_p^\dagger \rho_0 A_q)A_n^\dagger)\mathcal{G}_{qp}(t). \tag{49}$$

This equation has the structure of Eq. (3), i.e. of the final result of Grover and Silbey [1]. Now, because of the definition of $\mathcal{H}_1$ in (44), one can easily reveal that in (49), the second term on the right hand side (leading to γ_{mn}- as well as $\bar{\gamma}_{mn}$-coefficients in the Haken-Strobl parametrization) is really proportional to $\tilde{J}^2$. Finally, because of the same algebraic structure of the right hand side of (49) and that in (30), our definition (39) again takes place in the above parametrization scheme. Here, however, $\mathcal{H}_1$ is given as in (44), i.e. it has no diagonal elements. Thus, $\gamma_{mm} = 0$, in a full correspondence with the Grover and Silbey theory [1]. Detailed calculations based on projector (43) showing that in detail will be published elsewhere.

So, seemingly, we have got that rather some ambiguity (choice (43) with (44)) instead of (21) with (27)) is responsible for disappearance of the diagonal Haken-Strobl parameters γ_{mm}. This might lead to a seemingly provocative question: If in one (of two otherwise physically equivalent) set of equations, there are parameters γ_{mm} while in the second set (derived in a slightly different way for *the same quantities*) these parameters are absent, which is their physical significance? At the first sight, the situation reminds of an old problem whether the optical absorption on, e.g., molecules is to relaxed or unrelaxed states. For the latter problem, the answer is that we get the same result within the accuracy given by the energy uncertainty (including shift as well as the broadening) of energies of the unrelaxed states. If this analogy really applies here, one should be careful ascribing any deep physical meaning to these site-diagonal Haken-Strobl parameters γ_{mm}.

The real situation is, however, not so unclear as it might seem. Five sentences back, we have stressed the words *the same quantities*. In fact, we want to argue that the same (independent of the choice (43) with (44) instead of (21) with (27)) quantities in the two alternative formulations of the GSLE model are just the diagonal elements $\rho_{mm}(t) = P_m(t)$ (see (14) above) yielding the probabilities of finding the (bare as well as dressed) exciton at individual sites. For these quantities, the above provocative question is probably meaningful. On the other hand, the off-diagonal elements $\rho_{mn}(t)$, $m \neq n$ are appreciably influenced by the above choice. In particular, we argue that with the choice of (21) with (27), $\rho_{mn}(t)$ represents the *bare*-exciton density matrix while with (43) and (44), we are led to the *dressed*-exciton density matrix, i.e. to the Grover and Silbey parameters $\mathcal{G}_{nm}(t)$. This then fully explains all the analogies of the above second alternative of the GSLE model (with the choice (43) and (44)) and the theory by Grover and Silbey [1]. (At this point, similarities with infinite order theory by Čápek and Barvík [20] also suggesting the absence of the diagonal elements γ_{mm} are worth mentioning though this theory is formulated just for the diagonal elements of the bare- as well as dressed-exciton density matrix.) Simultaneously, this also explains the above differences between the SLE (or the first alternative of GSLE) and the Grover and Silbey theory [1].

At the end, the last and cardinal question remains: Which of the two groups of theories (Grover&Silbey, GSLE with choice (43) and (44) or [20] without any γ_{mm} but with the polaron renormalization (4) on one hand or the traditional SLE or GSLE with choice (21) with (27) yielding non-negligible γ_{mm} but no polaron renormalization on the other one) is thus more appropriate in real situations? Our answer is that if we were able to avoid approximations, all these approaches would necessarily be equivalent yielding the same result for corresponding quantities. (This is important when ascribing any physical meaning to γ_{mm}'s or the polaron renormalization (4).) Unfortunately, even formally identical approximations can yield different results in different schemes. So, with approximations, the answer must be looked for each case separately. For instance, preferential character of the Grover&Silbey-like theories in case of a strong diagonal exciton-phonon coupling is likely while in the opposite situation, the opposite is true.

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