

The instability in the long-time regime behaviour of a kinetic model

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Abstract

The relation between the infinite-time asymptotic regime behaviour of a Davies-like kinetic equation and the asymptotic behaviour of the nonapproximated reduced density matrix ρ is investigated. The asymptotic form of ρ determined from the second-order kinetic equation for some typical transfer model is found to be unstable with respect to higher-order contributions to the relaxation terms of the master equation. The relation between results obtained using the analysis of a power series in the energy domain and those given by Davies-like scaling will also be discussed.

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1. Introduction

There is a widespread opinion that solutions to kinetic equations naturally steer for the canonical distribution whenever the transfer rates are correctly calculated. In fact, such a statement was verified in the past for some not very complicated model systems in the van Hove (weak coupling) limit [1]. On the other hand, no general rigorous formulation was found so far in this direction and there are even some recent results, where not very complicated transfer phenomena models treated using generalized master equations display completely ‘noncanonical’ behaviour in the asymptotic regime [2, 3]. The cited papers use the rigorous Davies scaling theory [4, 5], but not necessarily the van Hove limit [6]. The main difference as compared to the van Hove is that what is scaled is not only the dynamics of the bath-induced relaxation, but also a part of dynamics of the system itself (as described by the Hamiltonian H_S of the system). This formal approach is physically reflected as ‘going beyond the weak-coupling limit’. A general motivation for such a choice of scaling is provided in [7, 8]. It is an attempt to describe a specific physical regime of the undisputable interest, the situation when the rates of the internal system dynamics are not infinitely faster than the rates of the bath-induced relaxation processes inside the system, but of a comparable magnitude.

One should be reminded of the fact that the van Hove limit means physically to decrease formally the system–bath coupling, reducing thus the rates of the bath-assisted processes. Thus, the bath-assisted processes are necessarily considered to be infinitely slower than those of the internal system dynamics. The very existence of such bath-assisted processes is then formally (though just in the lowest order) preserved by increasing simultaneously the time unit to infinity, in such a way that the product of the time unit and the squared system–bath coupling remains constant. Clearly, such a regime cannot be applied to the situation when the bath-assisted processes become commensurable with those of the internal system dynamics.

The modified Davies scaling [7], treating both the system–bath coupling and the terms in H_S on equal footing (as a scaled part of the total Hamiltonian), preserves the relative magnitude of such competing processes well. This outlines its physical motivation. One should realize here that in this scaling approach, the formally decreasing rates of the internal as well as bath-assisted processes are again compensated by the increase of the time units but not, as in the singular reservoir case [9, 10], by any simultaneous unphysical limit of, e.g. the bath spectrum. One could also comprehend such a scaling from another point of view. This approach may be followed as a useful way to calculate the system dynamics, when the system Hamiltonian H_S is complicated. In order to obtain the relaxation rate in the van Hove limit approach exactly, one must, in fact, be able to diagonalize H_S . But this case is not quite usual. Then one usually calculates the relaxation rate using some ‘dominant part’ of the system Hamiltonian, and then attaches the remaining terms, considered as not very strong perturbation. It is then understood as an approximate description (see, e.g., chapter XII, par 104 in [11]). The relation to the exact result can be obtained, e.g. by introducing a ‘nonstandard’ scaling. Such approximations provide further motivation of the present work.

The formal device for the treatment is a nonconvolution (convolutionless) generalized master equation (TCL-GME) using various scaling techniques in the present work. Starting from the GME power series in a scaling parameter we are going to demonstrate that though the scaling technique results are sometimes reflected as ‘exact’, they are, in fact, only the time-domain version of the finite (second) order power series in the energy domain. Consequently, Davies theorems do not reproduce the asymptotic results better than the analysis of the finite-order perturbational series of the GME coefficients.

The asymptotic state conditions in the TCL-GME formalism are finally reduced to a linear algebraic problem. We thus obtain the asymptotics of ρ as an eigenvector (in the Liouville space) related to the eigenvalue with the zero real part of a projected Liouville superoperator. Such a vector exists, this follows from the fact, that GME preserves the trace of the density matrix. Whenever just one such vector exists, it is usual to regard it as asymptotics of ρ of the system (on the grounds of the assumption that, for physical reasons, no solution increasing in the time infinity occurs and the other eigenvectors are related to the exponentially decaying solutions). However, this step is not justified from the point of view of the perturbation theory. If there is another eigenvalue with the real part only slightly different from zero (for example, it differs from zero as in the fourth-order in perturbation parameter), the result can substantially change after computing the fourth order terms in relaxation coefficients, and the change of the zero-eigenvector may be quite arbitrary. More precisely, let us designate the projected Liouvillean (for $t \rightarrow \infty$) evaluated to n th order $\mathcal{L}_{P,\infty}^n$. Moreover, we designate ρ_2, ρ_4, \dots the following vectors in the Liouville space of the system

$$\mathcal{L}_{P,\infty}^n \rho_n = 0.$$

We will argue that there is no sufficient reason, in our case, to believe that

$$\lim_{\lambda \rightarrow 0} \rho_2(\lambda) = \lim_{\lambda \rightarrow 0} \rho_4(\lambda).$$

We also show that such a phenomenon has its reflection in the Davies theorems concerning the solution of TCL-GME in the time domain [4, 5]. The Davies theorems state in a liberal transcription: ‘The evolution calculated in the second-order theory is a quite good approximation. For any finite interval of rescaled time and the limit of the scaling parameter λ going to zero, the second-order TCL-GME yields the correct result’. What is the problem: the ‘topology’ given by the Davies limit is too weak to distinguish between relaxation with rates proportional to $e^{-\lambda t}$ and the stationary solution whenever the allowed time interval is limited as in the Davies theory [1, 4, 5] by times proportional to λ^{-2} . In fact, the Davies theorems as well as any rigorous mathematics of this type remain unjustified in the infinite time domains. Often found applicability of kinetic theories beyond the so-called kinetic regime [12, 13], in particular in the dc limit, thus remains based on just a good belief.

Finally, let us make a brief comment concerning the relation to the van Hove limit. One could expect some objections with arguments such as the following: ‘You should not exaggerate the meaning of the above statements as no such crazy unstable behaviour was observed in the case of the van Hove limit. Perhaps the van Hove limit is in this sense correct. It thus provides the ‘proof’ that the canonical density matrix is always the proper asymptotics of the time evolution so that the only right way is to treat the system Hamiltonian without any scaling and to scale only system–bath coupling. The asymptotics of ρ is well known and the arbitrary physically correct model and its treatment must reproduce it’.

We do not consent to this opinion. Let us briefly sketch an easy argument against the correctness of such an argumentation. Consider a finite-dimensional linear operator with a twofold degenerate eigenvector. Then the degeneracy is broken introducing a slight difference in their eigenvalues (operating on the subspace of the ‘degeneracy’). We have two new nondegenerate eigenvectors, but the difference between their eigenvalues is small. If we further introduce a perturbation, it follows from the theorems of the perturbation theory that one finds the correction for the spectral decomposition of the perturbed operator as the power series in the neighbourhood of the eigenvalues. But the radius of convergence is intimately connected with the difference between the eigenvalues (e.g. [14, 15] for self-adjoint operators). In fact, the perturbational treatment is applicable if the perturbation is weaker than the eigenvalue difference [11]. But we treat just the opposite case. So we cannot agree with the attitude that the van Hove limit is resistant against the above problems. Moreover, our argumentation could be modified to apply for the case of an external field influence, where no ‘prescribed’ asymptotics is at hand.

2. Model

2.1. Hamiltonian

The system we will deal with is described by a model Hamiltonian

$$H = H_S + H_B + H_{S-B} \quad (1)$$

where

$$H_S = \lambda^2 J \hbar (c_0^\dagger c_1 + c_1^\dagger c_0)(b + b^\dagger) + \epsilon \hbar c_1^\dagger c_1 + \hbar \omega (b^\dagger + \gamma c_0^\dagger c_0)(b + \gamma c_0^\dagger c_0)$$

$$H_B = \sum_{k=1}^N \hbar \Omega_k B_k^\dagger B_k \quad H_{S-B} = \lambda \frac{1}{\sqrt{N}} \sum_{k=1}^N \hbar \Omega_k G_k (b^\dagger B_k + B_k^\dagger b).$$

At first, we comment on the part of the Hamiltonian, which represents the dynamics of the system with no attached bath. There are two sites labelled 0,1 here. The creation and annihilation operators $c_{0,1}^\dagger, c_{0,1}$ are related just to this site variable. As far as one particle

is considered we do not need to introduce (anti)commutational relations. Moreover, the vibrational levels in the harmonic-potential approximation are considered at each site. This potential is also described in the standard Fock formalism using creation and annihilation operators b^\dagger, b . These obey, according to their vibrational nature, bosonic commutational relations. Centres of the harmonic potential ascribed to different particle positions differ. This feature of the model is expressed as a polaron shift γ on site 0. The energy of the site 0 is taken as a zero-energy level. Furthermore, we allow a coherent transfer connected with the particle transition between the sites, which is described via the terms proportional to J .

The bath is represented by a set of N harmonic oscillators (B^\dagger, B). The system–bath interaction effects are caused by the last term of the Hamiltonian. In fact, we do not mean that the behaviour of the system (referred to later in the text) we have just introduced is intimately related to the specific form of the bath. The only important feature is that the system–bath coupling acts between vibration levels, so the leading terms of a relaxation tensor can only cause the relaxation between different vibrational levels (and of course, dephasing effects among these levels connected with this relaxation), but not incoherent particle transfers between sites 0 and 1. The problem we would like to examine has more general consequences. There is a combination of strictly coherent transfer processes (induced by H_S only) between particle sites as well as vibrational levels inside the system interfering with bath-assisted incoherent transfer processes between the same vibrational levels of the system. The point with respect to what follows below is that incoherent process coefficients in the relaxation tensor conform to the rules of canonical thermodynamic behaviour including detailed balance while, on the other hand, the coherent elastic processes break this behaviour (such processes are naturally symmetric). Moreover, in recent times, models analogical to (1) were reported [2, 16] to have behaviour in no sense close to the canonical one. The major question of the present paper is whether such calculations are sufficiently ‘rigorous’ in the infinite-time region.

2.2. Master equation

We outline the appropriate technical devices for any treatment of the open system interacting with the bath. The use of the wavefunction of the system is impossible, because such an object does not allow the introduction of any averaging procedure over the bath owing to its nonlinear relation to the measurable quantities. The appropriate theoretical object which enables removing any unnecessary information about details of the bath evolution (such information is unnecessary for arbitrary measurements on the system, i.e. quantities represented by operators operating on the Hilbert space of the system only) is the reduced density matrix of the system. Techniques to project off the bath variables are well known as generalized master equations (GME). Their application in the open system treatment is standard [17]. These equations have two conceptually different forms, the time-convolution (TC-GME) and time-convolutionless (TCL-GME) one. These forms are equivalent until we keep exact formulae; however, they can result in nonequivalent approximations. General reasons for the selection of one of the forms were extensively discussed (see some relevant papers [18, 19]). The works we refer to use TCL-GME; moreover, there are several other dominant reasons to prefer here the TCL-GME formalism.

1. The treatment of long-time asymptotic values is simpler in time local equations.
2. TCL-GME provides a definite order in the perturbation series (in time-nonlocal equations this point can be a little subtle). For TC-GME it seems to be sufficient to investigate only its Markov approximation. The relation between the Born–Markov approximation

of TC-GME and the second-order approximation of TCL-GME we would like to discuss elsewhere.

3. We expect the asymptotic solution to be stationary. So, there is, under the convolution integral, no time dependence except for memory, and the stationary condition becomes, in fact, in any case ‘convolutionless’.

However, the equivalent variants are to work with the Nakajima–Zwanzig identity [20–22] or in the Tokuyama–Mori formalism [23]. The Tokuyama–Mori formalism is used in this paper.

Further theory is formulated in the Liouville space (i.e. space of operators on the Hilbert space) derived from the Hilbert space we dealt with before. The set of all operators on the Hilbert space of the system is chosen as the set of observed quantities. We choose the projection superoperator (operator on the Liouville space) \mathcal{P} with the idempotency property $\mathcal{P}^2 = \mathcal{P}$ in the following way:

$$\mathcal{P} \dots = \sum_{\alpha\gamma} |\alpha\rangle\langle\gamma| \text{Tr}(|\gamma\rangle\rho_B\langle\alpha| \dots).$$

Here ρ_B is the initial density matrix of the bath. This choice enables us later to remove the initial condition term. Then the Heisenberg equations of motion for operators are reduced to the set of equations for matrix elements of the system density matrix called the Tokuyama–Mori generalized master equation:

$$\frac{d}{dt} \rho_{\alpha\gamma}(t) = \sum_{\delta\beta} i\omega_{\alpha\gamma,\delta\beta}(t) \rho_{\delta\beta}(t) + f_{\alpha\gamma}(t) \quad (2)$$

with the following exact expressions for coefficients:

$$i\omega_{\alpha\gamma,\delta\beta}(t) = i\text{Tr}(|\delta\rangle\rho_B\langle\beta|\mathcal{L}(|\gamma\rangle\langle\alpha|)) - \text{Tr}\left(|\delta\rangle\rho_B\langle\beta|\int_0^t e^{-i\mathcal{L}\tau}\mathcal{P}e^{i\mathcal{Q}\mathcal{L}\tau}d\tau\right. \\ \left.\times\left[1 - \mathcal{Q}\int_0^t e^{-i\mathcal{L}\tau}\mathcal{P}\mathcal{L}e^{i\mathcal{Q}\mathcal{L}\tau}\right]^{-1}\mathcal{Q}\mathcal{L}(|\gamma\rangle\langle\alpha|)\right) \quad (3)$$

and

$$f_{\alpha\gamma}(t) = \text{Tr}\left(\varrho(0)e^{i\mathcal{Q}\mathcal{L}t}\left[1 - \mathcal{Q}\int_0^t e^{-i\mathcal{L}\tau}\mathcal{P}i\mathcal{L}e^{i\mathcal{Q}\mathcal{L}\tau}d\tau\right]^{-1}\mathcal{Q}i\mathcal{L}|\gamma\rangle\langle\alpha|\right) \quad (4)$$

where $\mathcal{L} \dots = \frac{1}{\hbar}[H, \dots]$ is the Liouville superoperator, $\mathcal{Q} = 1 - \mathcal{P}$. With the initially statistically independent system and the bath and, simultaneously, the initial bath density matrix $\text{Tr}_S \varrho(t=0)$ equal to ρ_B , the inhomogeneous initial condition term $f_{\alpha\gamma}(t)$ in (4) and (2) equals zero. Further, the initial bath density matrix is assumed to be canonical

$$\rho_B = \frac{e^{-\beta_\tau H_B}}{\text{Tr}_B e^{-\beta_\tau H_B}}.$$

So, the coefficients $\omega_{\alpha\gamma,\delta\beta}(t)$ are the only ones to calculate. The part of Hamiltonian (1) independent of the scaling parameter λ is designated as H_0 (and simultaneously the related Liouville superoperator as \mathcal{L}^0) and the power series is provided in the perturbational parameter. Up to the second order it yields

$$i\omega_{\alpha\gamma,\delta\beta}(t) = i\text{Tr}(|\delta\rangle\rho_B\langle\beta|\mathcal{L}(|\gamma\rangle\langle\alpha|)) - \text{Tr}\left(|\delta\rangle\rho_B\langle\beta|\int_0^t e^{-i\mathcal{L}^0\tau}\mathcal{P}\mathcal{L}e^{i\mathcal{Q}\mathcal{L}^0\tau}d\tau\mathcal{Q}\mathcal{L}(|\gamma\rangle\langle\alpha|)\right) \\ \equiv -i\mathcal{L}_{\alpha\gamma,\delta\beta}^c - R_{\alpha\gamma,\delta\beta}. \quad (5)$$

For further development we build an appropriate base in the Hilbert space of the system. We label each base vector with two indices; the first one refers to the site variable, the second one to the vibrational level. Two different vibrational states (normal and polaron shifted) are introduced,

$$|\mu\rangle = \frac{1}{\sqrt{\mu!}}(b^\dagger)^\mu|0\rangle \quad |\mu'\rangle = \frac{1}{\sqrt{\mu'!}}(b^\dagger + \gamma)^\mu|0'\rangle \quad |0'\rangle = \exp \gamma(b - b^\dagger)|0\rangle.$$

These vectors in the factorspace of vibrational states diagonalize the vibrational part of the Hamiltonian over site 1 or 0, respectively. We specify the base of the Hilbert space of the system we will refer to as

$$|1\mu\rangle \equiv |1\rangle|\mu\rangle \quad |0\mu\rangle \equiv |0\rangle|\mu'\rangle.$$

We explicitly emphasize that in the second definition on the left-hand side, there is no prime present. A further step in the development of the theory is to take time limit of the Tokuyama–Mori coefficients to infinity ($t \rightarrow \infty$). This step is usually considered as omitting the short-time transient memory effects. In agreement with the fact that we are interested in the infinite-time limit, we have no problem in introducing this step and our formulae remain exact. We start the evaluation of the coefficients in (5) with the relaxation tensor R (the second term on the right-hand side of (5)) describing relaxation processes. It yields

$$\begin{aligned} R_{1v,1\mu,1\alpha,1\beta} &= R_{0v,0\mu,0\alpha,0\beta} \\ &= \lambda^2 \frac{\pi}{N} \sum_k \Omega_k^2 G_k^2 \delta(\omega - \Omega_k) \{ \delta_{\alpha v} \delta_{\beta \mu} [n_k(\mu + v + 2) + (n_k + 1)(\mu + v)] \\ &\quad - 2\delta_{v+1,\alpha} \delta_{\mu+1,\beta} (n_k + 1) \sqrt{(\mu + 1)(v + 1)} - 2\delta_{v-1,\alpha} \delta_{\mu-1,\beta} n_k \sqrt{\mu v} \} \\ R_{0v,1\mu,0\alpha,1\beta} &= \lambda^2 \frac{\pi}{N} \sum_k \Omega_k^2 G_k^2 \delta(\omega - \Omega_k) \{ \delta_{\alpha v} \delta_{\beta \mu} [n_k(\mu + v + 2) + (n_k + 1)(\mu + v)] \\ &\quad - 2\delta_{v+1,\alpha} \delta_{\mu+1,\beta} (n_k + 1) \sqrt{(\mu + 1)(v + 1)} - 2\delta_{v-1,\alpha} \delta_{\mu-1,\beta} n_k \sqrt{\mu v} \\ &\quad + \gamma [\delta_{\mu-1,\beta} \delta_{v,\alpha} n_k \sqrt{\mu} - \delta_{v+1,\alpha} \delta_{\mu,\beta} (n_k + 1) \sqrt{(v + 1)} \\ &\quad + \delta_{v,\alpha} \delta_{\mu+1,\beta} (n_k + 1) \sqrt{(\mu + 1)} - \delta_{v-1,\alpha} \delta_{\mu,\beta} n_k \sqrt{v}] \} \end{aligned} \quad (6)$$

$$R_{1v,0\mu,1\alpha,0\beta} = R_{0\mu,1v,0\beta,1\alpha}^*$$

where n_k designates the equilibrium mean number of phonons

$$n_k = \langle B_k^\dagger B_k \rangle = [\exp \hbar \beta_T \Omega_k - 1]^{-1}. \quad (7)$$

The remaining coefficients equal zero. The last equality in (6) is only the consequence of the fact that the density matrix is self-adjoint. We attach a brief comment concerning the relaxation tensor. The relaxation coefficients with identical site indices are, in fact, independent of the site index but one must have in mind the difference in connected vibrational bases that we defined above. If one omits for a while the coherent processes described by the first term in (5) and the relaxation is considered only at one site, the process steers for the canonical density matrix of the oscillator and the behaviour is qualitatively compatible with other widely used types of relaxation (Landau–Teller relaxation [24]). It is worth noting that no direct relaxation coefficients responsible for the dephasing decay of $\rho_{0\alpha,1\alpha}$ appear. In particular, in the case $\gamma = 0$ one can verify that $\sum_\alpha \rho_{0\alpha,1\alpha}$ is preserved. Such decay, if present here, must come from more complicated effects of competition between, and collaboration of the coherent and incoherent channels.

The first (coherent) term in (5) is formed by the matrix elements of the internal system Hamiltonian

$$\hbar \mathcal{L}_{i,j,l,m}^c = \langle i | H_S | l \rangle \delta_{j,m} - \delta_{i,j} \langle m | H_S | j \rangle.$$

3. The asymptotic regime investigation

3.1. Numerical analysis of asymptotic spectrum

In the previous section we have prepared all the important pre-calculations, which are standard. The complicated problem of the time development given by the open system Hamiltonian (1) was reduced into a linear time-local problem formulated in the Liouville space of the system. In this subsection the infinite time limit of the solution to the second-order approximation of Tokuyama–Mori equation (5) is investigated. As a consequence of the time-independent character of the coefficients calculated above, theorems of linear algebra yield a simple picture of the solution. The number of vibration levels is restricted to a finite value for simplicity. This step cannot have very important physical relevance. In fact, the restriction can be introduced in the Hamiltonian (1) as an additional model assumption, then this step is exact. Consequently, the solution of the finite set of linear differential equations is given by a linear combination of exponential functions with possible polynomial prefactors and arguments consisting of products of time with eigenvalues of the matrix problem

$$\sum_{\delta,\beta} \{-i\mathcal{L}_{\alpha\gamma,\delta\beta}^c - R_{\alpha\gamma,\delta\beta}\} \rho_{\delta,\beta}(\eta) = \eta \rho_{\alpha\gamma}(\eta). \quad (8)$$

For physical reasons, we assume that no terms increasing without limits in the time infinity occur. So, no eigenvalue of (8) can have the positive real part; moreover, no eigenvalue with the real part equal to zero is connected to the polynomial function prefactor. The further comment is that all the terms related to eigenvalues with the negative real part fall to zero with time going to infinity. So, the only eigenvalues relevant for the infinite-time limit are those with the real part equal to zero. We call $\mathcal{S}^{(n)}(\lambda)$ subspace spanned on the kernel subspaces connected with eigenvalues with the zero real part of the n th order approximation of the projected Liouville superoperator (3). Moreover, we use the same symbol without λ -dependence for the following limit subspace

$$\mathcal{S}^{(n)} \equiv \lim_{\lambda \rightarrow 0} \mathcal{S}^{(n)}(\lambda).$$

One zero-eigenvalue eigenvector always exists because of the identity

$$\sum_{\alpha} \{-i\mathcal{L}_{\alpha\alpha,\delta\beta}^c - R_{\alpha\alpha,\delta\beta}\} = 0 \quad (9)$$

stemming from (3) and implying that the time-development, as described by (2), preserves total probability $\sum_{\alpha} \rho_{\alpha\alpha}(t)$. This identity is preserved in potentially any order of expansion of the above coefficients. Hard difficulties occur in establishing asymptotic treatment whenever $\dim \mathcal{S}^{(2)} > 1$. Then the asymptotical solution depends on the initial conditions; moreover, the deficiency concerning the justification of Born approximation and long-time limit of relaxation coefficients becomes apparent.

Therefore, we ask for evidence of the nondegeneracy of $\mathcal{S}^{(2)}(\lambda)$. This is usually done by the scrutiny of the simulation of the system time evolution of ρ in a given approximation starting from different initial conditions, and a decision on whether the asymptotics of ρ depends on initial conditions or not. As we are interested in the long-time domain only we prefer another equivalent method. It is a careful evaluation of eigenvalues and eigenvectors. We have used this variant of calculation for many parameters of model (1), and we found the zero eigenvalue to be almost always nondegenerate (with exception of very special and physically understandable choices). The existence of more than single zero-eigenvalue solutions to (8) was also recently rejected by direct numerical studies for a parallel model reported in [3].

Thus, we have some reason to believe, in the most usual variant, in the nondegeneracy of the zero-eigenvalue eigenvector and, thus, in the unique asymptotic form of the density matrix

as prescribed by the finite-order perturbation theory (in finite coupling to the bath) extended to the long-time region. The question of the presence of near-to-zero eigenvalues of (8) is, however, a somewhat different problem.

In particular we observe another problem which should be solved: Is the nondegeneracy ($\dim \mathcal{S}^{(2)} = 1$) described above really sufficient evidence for the stability of the asymptotic behaviour against higher-order contributions in the power series of (3), which is usually silently assumed? Let us consider that there is a further eigenvalue η which quickly approaches zero when the perturbational parameter is limited to zero $\lambda \rightarrow 0$. If the dependence

$$\eta(\lambda) = -\text{const} \times \lambda^k \quad (10)$$

in the neighbourhood of $\lambda = 0$ has an exponent k , we can imagine such a k th order correction of (5) which causes the strict instability $\mathcal{S}^{(n)}$ against n . This of course also means the instability of $\mathcal{S}^{(n)}(\lambda)$ in the neighbourhood of $\lambda = 0$. In other words, such a correction changes the asymptotic behaviour in a very dramatic way. Our approximation is of the second order (it has a fourth-order correction). So we have to take care of near-to-zero eigenvalues with $k \geq 4$.

This problem is considered for our model (1) in approximation (5). We numerically treated the spectrum of the second-order approximation of the Liouville superoperator (8) for a number of parameters of the model. Of course, the results appreciably depend on the actual parameters, but we can make some conclusions quite generally. Some eigenvalues have their real part quite close to zero, and more importantly, the latter fall very rapidly to zero when the perturbational parameter is limited to zero. This point need not be necessarily visible for ordinarily used fixed values of λ .

The most important property of such eigenvalues is their behaviour in the neighbourhood of $\lambda = 0$. We tried to find the exponent k from (10) for the second smallest eigenvalue η_1 , which is near to zero, for our particular problem. We examined the $\eta_1(\lambda)$ dependence for a number of parameters and in figures 1 and 2, typical results of our treatment are shown. The actual model parameters are given in figure captions. In order to envisage a polynomial dependence we draw $-\log \lambda$ versus $-\log(-\eta_1)$ graph and its derivative. One can easily realize from (10) that coefficient k is given by a tangent in the asymptotical region in figure 1, and by value of the asymptotics in figure 2 (see the 'figure caption' for details). The imaginary part of η_1 is 0 within numerical accuracy (13 digits). The main results may be summarized as follows:

- Numerically, we have verified that the zero eigenvalue is not degenerated. It proves the unique asymptotics of (5).
- The linearity of figure 1 in the asymptotical region proves the anticipated formula (10) and that, more importantly, we investigated the region of λ where the asymptotical term dominates.
- We determined numerically the exponent to be equal to 6. Considering the exponent to be unavoidably a rational number corresponding to theorem XII.2 of [14], we conclude that there is an eigenvalue exactly proportional to λ^6 .

The reader interested in details concerning the numerical implementation is referred to appendix A.

3.2. Analytical treatment of the stationary condition

In this subsection we only care about those results, which can be proved to be stable against the arbitrary fourth-order correction of (5). First of all, we are not going to perform the real evaluation of higher order contributions here. It appears to be straightforward, but technically extremely extensive calculation. We take into account an arbitrary possible fourth order

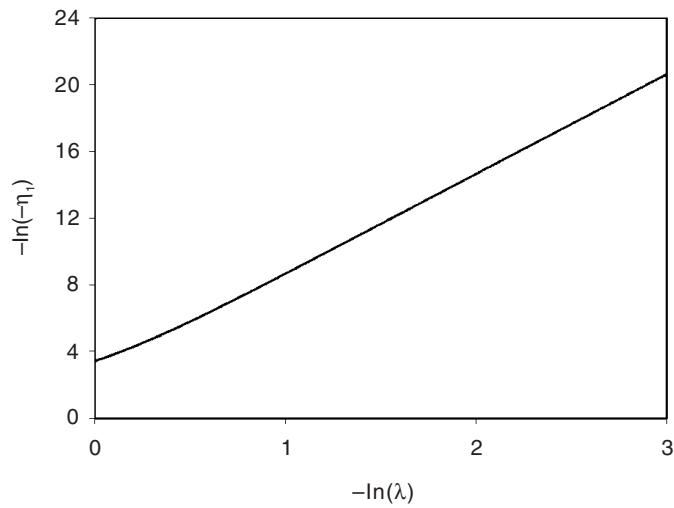


Figure 1. We plot $[-\ln(-\eta_1)]$ versus $[-\ln(\lambda)]$ (η_1 being the second smallest, in the absolute value, eigenvalue of the projected Liouvillean (8) for model (1) in the text. One can prove that the order of leading term of $\eta_1(\lambda)$ dependence is given by the steepness of this graph in the $[-\ln(\lambda)] \rightarrow \infty$ region. The polynomial character of the dependence (10) is proven by the linearity of the graph in this region. Model parameters: $\epsilon = 0.2, \omega = 1.0, \gamma = 0.2, J = 0.1, \hbar\beta_T = 1.0, \frac{\pi}{N} \sum_k \Omega_k^2 G_k^2 \delta(\omega - \Omega_k) = 1.0$. The given density of states at $\Omega = \omega$ enables the straightforward calculation of relaxation tensor with respect to (7): $\frac{\pi}{N} \sum_k \Omega_k^2 G_k^2 \delta(\omega - \Omega_k) n_k = \frac{1}{e-1}$ and $\frac{\pi}{N} \sum_k \Omega_k^2 G_k^2 \delta(\omega - \Omega_k) (n_k + 1) = \frac{e}{e-1}$.

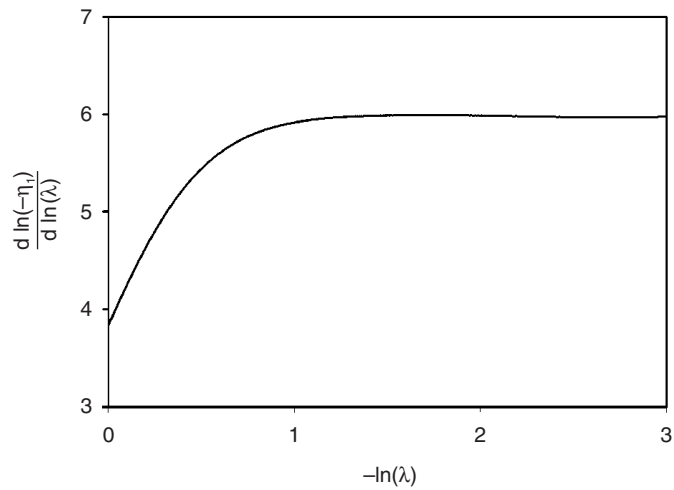


Figure 2. The derivative $\frac{d \ln(-\eta_1)}{d \ln(\lambda)}$ of figure 1 versus $[-\ln(\lambda)]$. One can more precisely see the linearity of figure 1. For $\lambda \leq e^{-1}$ the derivative is nearly constant, which again proves the polynomial character of (10). Moreover, we clearly see the leading term order k in (10) to be equal to 6. (Limit of the graph in the $[-\ln(\lambda)] \rightarrow \infty$ region.) The parameters are as above.

result. Several ways are possible for the analytical investigation. For example, one may discuss exactly how some eigenvalue depends on the perturbational parameter, in parallel to

the previous subsection but it is not an analytical work ‘with pen and paper’ only. The way we are going to follow is less ambitious. We take care only of strictly zero eigenvalues $\eta = 0$ (with no imaginary part). The point is to expand explicitly the asymptotic value of the density matrix into the power series. As we have anticipated, the right-hand side of eigenvector equation (8) is substituted by zero. The important point is that any coefficient can have a correction \mathcal{O} in the fourth order. The only accepted results are those that are independent of \mathcal{O} ,

$$\sum_{\delta,\beta} \left\{ -i\mathcal{L}_{\alpha\gamma,\delta\beta}^c - R_{\alpha\gamma,\delta\beta} + \lambda^4 \mathcal{O}_{\alpha,\gamma,\delta\beta} \right\} \rho_{\delta,\beta}(0) = 0 \quad (11)$$

$$\rho(0) = \sum_{i=0}^{\infty} \lambda^i \rho^{(i)}. \quad (12)$$

Consequently, only the zeroth order of (11)

$$\sum_{\delta,\beta} -i\mathcal{L}_{\alpha\gamma,\delta\beta}^{c(0)} \rho_{\delta,\beta}^{(0)} = 0$$

and the second order of (11)

$$\sum_{\delta,\beta} \left\{ -i\mathcal{L}_{\alpha\gamma,\delta\beta}^{c(2)} - R_{\alpha\gamma,\delta\beta}^{(2)} \right\} \rho_{\delta,\beta}^{(0)} + \sum_{\delta,\beta} -i\mathcal{L}_{\alpha\gamma,\delta\beta}^{c(0)} \rho_{\delta,\beta}^{(2)} = 0$$

form the relevant system of conditions. The reader is entreated for the comprehension of the delicate but constitutive difference between (11) and $\lambda \rightarrow 0$ limit of (8).

The central question is whether a uniquely given solution is obtained at least in the zero-order (in the density matrix series $\rho^{(0)}$). If not, then obtaining a unique result by calculation omitting higher-order contributions to the GME coefficients is irrelevant. One should realize that such a result is equivalent to the statement that there is another eigenvalue of (8) near zero (differing from 0 in the fourth or higher order). For simplicity, we exclude some incidental degeneracies by the requirement

$$\epsilon \neq s \cdot \omega$$

for s being an arbitrary integer. Application of the thesis formulated above yields: for $i \neq j$ (either in the site or vibrational index)

$$\rho_{i,j}^{(0)} = 0$$

while otherwise

$$\rho_{a\alpha,a\alpha}^{(0)} = C_a \left(\frac{n}{n+1} \right)^\alpha. \quad (13)$$

C_0, C_1 are two arbitrary constants. (We bear in mind that we must normalize the density matrix, so in fact, $C_0 + C_1 = (n+1)^{-1}$.) We designated

$$n = n(\Omega_k)|_{\Omega_k=\omega} = [\exp \hbar\beta_T\omega - 1]^{-1}.$$

Note that according to the Boltzmann distribution

$$\frac{n}{n+1} = e^{-\hbar\beta_T\omega}.$$

For the second-order result $\rho^{(2)}$, we obtain only a partial result,

$$\begin{aligned} \rho_{a\alpha,a\beta}^{(2)} &= 0 \quad \alpha \neq \beta \\ \rho_{0\alpha,1\beta}^{(2)} &= J[\sqrt{\beta}\langle\alpha'|\beta-1\rangle + \sqrt{\beta+1}\langle\alpha'|\beta+1\rangle] \frac{C_0 e^{-\hbar\alpha\beta_T\omega} - C_1 e^{-\hbar\beta\beta_T\omega}}{\omega(\alpha-\beta) - \epsilon}. \end{aligned} \quad (14)$$

The decision about the asymptotic is disabled, because there are two arbitrary constants C_0, C_1 . Let us repeatedly note that whenever \mathcal{O} is specified the result can be given uniquely. For example, $\lambda^4 \mathcal{O} = 0$ refers to the case we numerically treat in the previous subsection and we have seen that there was only one solution to (8). The results of (8) and (11) do not contradict, rather they illustrate the deficiency of the second-order approximation from different angles. We do not calculate explicitly the fourth order but depending on this result, result (13) can be obtained uniquely. Furthermore, the eigenvector corresponding to the near-to-zero eigenvalue from the previous subsection is related to the second independent solution in (13). This relates the results of these parts to the previous discussion.

The asymptotic distribution among the sites in the second-order theory is not credibly described on reflection (13); on the other hand, the vibrational level asymptotics is known and the results respect the canonical prescription. Note that our numerical calculations indicate further eigenvalues with a rapidly falling real part that lie in the neighbourhood of some imaginary numbers. The common feature is that the asymptotics of the particle distribution between sites is not well calculated. The only condition for the zeroth-order diagonal terms is balance equation given from relaxation among vibrational levels as follows from the detailed study of (11). The J -dependent terms in fact only cause appearance of covalent bonds in the second order. This situation is widely typical for similar Hamiltonians which combine coherent transfer among sites with relaxation on the sites [3, 16]. Note towards another type of scaling: if we scale J proportional to λ then our results will be more comprehensive but in the main conclusion not different. Nor here can we find asymptotics—see appendix B.

3.3. Relation to the Davies limit

Davies in his works built up the rigorous mathematical base for nonconvolution master equations. He proved some rigorous theorems for correctness of the solution one obtains using the second-order approximation of TCL-GME. We do not want, however, to take into question his rigorous arguments, but we warn about their not very high power (applicability) in some particular cases. Let us repeat the main statement for correctness of the master equations which Davies proved [1, 4, 5]:

$$\lim_{\lambda \rightarrow 0} \max_{\tau \in (0, \tau_0)} |\rho(\lambda^{-2}\tau) - \rho^{(\text{GME})}(\lambda^{-2}\tau)| = 0. \quad (15)$$

(We omit assumptions of that theorem, because they have no relation to our problem, and they are of mathematical importance only.) This result is sometimes referred to as the proof of GME correctness. However, we must ask which quantities are really well guaranteed by (15). The topology (on the space of one parameter, i.e. λ -dependent time-evolution of the density matrix) induced by the Davies limit is quite weak. One can prove that the fourth-order fall-off $\exp(-\lambda^4 t)$ (i.e. eigenvalue proportional to λ^4) is not distinguished from 1. Compare, e.g. (15) with a trivial statement

$$\begin{aligned} \mathcal{F}(\tau) &= e^{-\lambda^4 \tau} \\ \lim_{\lambda \rightarrow 0} \max_{\tau \in (0, \tau_0)} |\mathcal{F}(\lambda^{-2}\tau) - 1| &= \lim_{\lambda \rightarrow 0} \max_{\tau \in (0, \tau_0)} |e^{-\lambda^2 \tau} - 1| = \lim_{\lambda \rightarrow 0} |e^{-\lambda^2 \tau_0} - 1| = 0. \end{aligned}$$

In any case, we cannot decide about the right asymptotic value on the base of Davies limit theorems, if there is a slow fall-off to the GME asymptotic solution simply because (15) does not allow us to say anything about real infinite time limit (note that τ_0 in (15) is finite). We can show at this point the connection with the nonunique result (13) which we found in the previous subsection. We have shown that two linear independent solutions fulfil the equation

$$\sum_{\beta, \delta} \{-i\mathcal{L}_{\alpha\gamma, \delta\beta}^c - R_{\alpha\gamma, \delta\beta}\} \rho_{\delta, \beta} = 0$$

up to second order in λ . Anyway arbitrary choice of C_1, C_0 in (11) yields

$$\sum_{\beta, \delta} \{-i\mathcal{L}_{\alpha\gamma, \delta\beta}^c - R_{\alpha\gamma, \delta\beta}\} \rho_{\delta, \beta} = \mathcal{O}(\lambda^2).$$

So, we are able to introduce such a fourth-order ‘perturbation’ $\lambda^4 \delta\mathcal{L}$ of coefficients $\omega_{\alpha\gamma, \delta\lambda}$ in (3) that arbitrary choice of C_0, C_1 in (13) will provide the asymptotic value (13) for the related kinetic equation. Moreover, the new perturbed dynamics

$$\rho^{(4)}(t) = \exp[(-i\mathcal{L}^c - R - \lambda^4 \delta\mathcal{L})t] \rho(0)$$

satisfies the same condition as (15)

$$\lim_{\lambda \rightarrow 0} \max_{\tau \in (0, \tau_0)} |\rho(\lambda^{-2}\tau) - \rho^{(4)}(\lambda^{-2}\tau)| = 0 \Leftrightarrow \lim_{\lambda \rightarrow 0} \max_{\tau \in (0, \tau_0)} |\rho(\lambda^{-2}\tau) - \rho^{\text{GME}}(\lambda^{-2}\tau)| = 0.$$

So, the consequences of Davies theorems are not different from the conclusions of the above section concerning the accuracy of the second-order TCL-GME solution. A question remains: what is the right $\rho(t = \infty)$? Actually we must admit that this question remains open (see page 156 of [1]). We are even not completely sure whether the density matrix of the system (in the particular physical regime) really has any asymptotics at all. The resolution of the deficiency can look straightforwardly: carry out the higher order calculation. We warn of possible difficulties.

1. The calculation of higher-order terms in (3) is technically very complicated. In fact, nobody (as far as we know) has carried it out up to now.
2. As seen from above, the resolution can require calculation up to higher-order terms than one can imagine. In fact, our opinion is that the sixth order could probably be the essential one. This statement we are going to document in our future work.
3. Some conceptual problems may occur. For instance, many years were spent in establishing the standard form of the second-order approximation.

3.4. Physical consequences and conjectures on the mechanism

A few words concerning the physical interpretation and implications are relevant, because it seems to be quite unusual that processes which could be usually considered as slow can have a particularly important role in forming such a basic quantity such as the asymptotical density matrix. One should be suspicious with respect to vague terms ‘slow, weak, physically unimportant’, etc. The transfer of dynamical strength arguments is not the best argument to infer the asymptotical form of the density matrix.

Physically, one possible way of viewing the above result is to discuss the role of the above additional eigenvalues of (8) upon increasing time in formulae determining asymptotic form of ρ . Inspection of, e.g. (15) shows that arbitrarily small (in small parameters of the problem) but nonzero eigenvalues that do not enter the Davies analysis could in principle become relevant in the long-time domain. Thus, greater-than-usual care in methods of determination of the asymptotic form of the density matrix should in general be required.

With respect to our particular model: it seems that the direct second-order TCL-GME treatment of the coherent transfer is not adequately justified in the long-time regime, though this channel is important at short times. We see a possible connection with its off-energy-shell nature. The complicated interplay between the coherent transfer and the bath-induced decoherence treated parallel here describes a process complying with the energy conservation law. We consider the instability found as a residue of the reflection of these processes as competing ones, i.e. treated in the leading order of a particular process, rather than an integrally collaborating process pointing out investigations in adequately higher order.

This whole compound process is responsible for forming the asymptotical state, and an approximative decomposition is consequently paid for in the proved mathematical deficiency of the result obtained. The difference in index (site versus vibrational) characterizing the particular transfer channel is responsible for the apparent manner—instability, not only corrections—in which the problem appeared.

We are of the opinion that only the calculations that provide a basic analysis of these composed processes could give mathematically sounder predictions of the asymptotical state. This is, however, rather a speculation. A detailed physical comprehension of the subject involves simplifications of the model that is in the course of development.

4. Conclusions

The correctness of an asymptotic time behaviour treatment was examined. General consequences of problems encountered on the way were illustrated on one particular case of a two-site problem considering a Hamiltonian which combines the vibrational relaxation on one site with the coherent transfer between the sites. Attention was focused on the perturbational treatment using the TCL-GME technique, where the asymptotically stationary solution which is independent of the initial density matrix of the system is usually found. However, in the physical regime of comparable fast bath-induced and coherent transfer, formally connected with the particular perturbation scheme of the treatment we pointed out the deficiency of ordinarily used second-order approximation. We observed a very slow decay of one solution of the TCE-GME different from the stationary one, connected with an eigenvalue in the spectrum of the projected Liouville superoperator, which approaches to zero with the perturbational parameter as λ^6 . As a consequence, the asymptotic state cannot be determined keeping in mind the possible influence of the higher-order (in the perturbational series) contributions to (3). More precisely, there is, in general, a whole linear space (with dimension greater than one) of spurious density matrices, which can appear as a leading term in the perturbational series of the true asymptotic (stationary) density matrix. This fact can also be reflected in the Davies limit theorems. We found that the topology provided by Davies limit is too weak to separate the stationary solution from slowly decreasing solutions. So the Davies theorems hold good but in this case do not guarantee correctness of any evaluation of $\rho(t = \infty)$.

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Appendix A. Numerical implementation

Some readers would probably like to judge the credibility of the numerical results, so we add some details concerning the connected numerical implementation. There are two points we are going to comment on more widely.

A.1. Reducing the Hilbert space of system to finite dimension

The Hilbert space of the system has to be reduced to the finite-dimensional one \mathcal{H}_S^R for the numerical implementation. Our \mathcal{H}_S^R consists of the linear extension of vectors $|1\rangle|\mu\rangle, |0\rangle|\mu'\rangle, \mu, \mu' \in 0, \dots, q$. Any reduction involves some attention in order to hold the physically important properties of the projected Liouvillean, namely (9). The connected difficulties were referred to in [16] where the base $|i\rangle|\mu\rangle, i \in \text{set of sites}, \mu \in 0, \dots, q$ were chosen and the relaxation tensor over the polaron-shifted states had to be *ad hoc* ‘corrected’. The reduction of the relaxation tensor on the finite number of levels is straightforward in our base. All terms of the relaxation tensor have a physical interpretation—they are connected with some transition from a level to a level—we remove those ones connected with the transition to (from) the ‘more than q -excited’ levels. The implementation of \mathcal{L}^c term is described below.

There is a wider physical background of our choice of \mathcal{H}_S^R . The internal problem of choosing \mathcal{H}_S^R according to [16] stems from the fact that the polaron-shifted level does not belong to \mathcal{H}_S^R . The pure projection of shifted states on $\mathcal{H}_S^{R1} \equiv \oplus_{\mu} |\mu\rangle$ then conserves neither the norm nor the angles between the polaron-shifted levels. Consequently, the projection of the relaxation tensor on the restricted base according to standard rules does not hold (9). We suggest identifying the polaron state $|\mu'\rangle$ with some vector $|\mu'\rangle^R$ in the restricted space \mathcal{H}_S^{R1} in a way which conserves the norm and the angles between the polaron states and moreover that is near to the simple projection at least for the low polaron levels. Such a method is Gramm–Schmidt orthonormalization process (see [25]) with the projection of vectors connected with shifted levels

$$C_{\mu} |\mu'\rangle^R = \sum_{v=0}^q |v\rangle \langle v|\mu'\rangle - \sum_{\eta=0}^{\mu-1} \sum_{v=0}^q |\eta'\rangle^R \langle \eta'|^R |v\rangle \langle v|\mu'\rangle$$

with a normalization constant C_{μ} chosen in order to fulfil $\langle \mu'|^R |\mu'\rangle^R = 1$. This method provides a general approach for the related phenomena with additional advantages:

- It leaves the most important low levels as undistorted as possible. $|\mu'\rangle^R$ converges to $|\mu'\rangle$ with increasing q . It suggests a simple orientation for the selection of available q . The choice is reasonable when an increase of q does not change the result appreciably.
- In the reduced Hilbert space \mathcal{H}_S^{R1} the orthonormal relation and the completeness relation remain valid,

$$\langle v'|^R |\mu'\rangle^R = \delta_{\mu,v} \quad \sum_{\mu=0}^q |\mu'\rangle^R \langle \mu'|^R = 1 \text{ on } \mathcal{H}_S^{R1}.$$

It also implies keeping (9) for relaxation over the shifted site.

- As far as a relaxation process over one site is considered, the distortion coming from the projection procedure is unimportant. We easily works in the Hilbert space $|1\rangle|\mu\rangle$, and $|0\rangle|\mu'\rangle, \mu, \mu' \in 0, \dots, q$, respectively.
- The identification of the reduced Hilbert spaces of the ‘normal state’ and the reduced shifted state enables potentially the reduction of information about site-oscillator correlations.

The only thing that remained to be specified is the implementation of \mathcal{L}^c term. We suggest here transferring the matrix elements from the base $|1\rangle|\mu\rangle, |0\rangle|\mu'\rangle$ to the reduced base $|1\rangle|\mu\rangle, |0\rangle|\mu'\rangle^R, \mu, \mu' \in 0, \dots, q$ without changes. We emphasize: though the just described implementation is only approximate with regard to the introduced model (1), the restriction to the finite number of levels and also the distortion of \mathcal{L}^c terms can be introduced in (1). Consequently, the implemented master equation is exact for an open model which is

near to the introduced one. This comprehension is advantageous because it suggests that the deviations against $q \rightarrow \infty$ are not errors summing together through the computation (e.g. numerical derivation in figure 2). Of course we must use constant \mathcal{H}_S^R .

A.2. Implementation of spectral analysis and error estimation

All the spectral analysis was implemented in Fortran 90 with complex double precision. We controlled the exact validity of (9) as far as the double precision representation in 2×64 bits enables. This care is important because it proves the existence of the zero eigenvector (the stationary state of the density matrix). For resolving the spectrum the standard routine DEVCCG from Microsoft IMSL library (see also [26]) with some additional control of errors was used. One simply estimates the error of the zero eigenvalue. We know the exact eigenvalue, further we know also the left eigenvector from (9). All the referred results (concerning zero eigenvalue) had the accuracy of the order of 10^{-13} . The estimation of the eigenvalues was stopped when the nearest eigenvalue approached the zero eigenvalue at the distance of the order of 10^{-8} . The ratio between the greatest observed error of the zero eigenvalue and the second smallest eigenvalue that we referred to is therefore of the order of 10^{-5} . Further, we observed the second smallest eigenvalue to have the imaginary part equal to zero with the accuracy of 13 digits, which is the order of numerical errors. However, we have no fundamental proof of such a statement, but at least the imaginary part of the second smallest eigenvalue is negligible. Also the sign of the real part of the remaining eigenvalues and further physically important quantities were checked. One can consider 10^{-13} as a reasonable estimation of the numerical error (in eigenvalue). The second region of our check consists in keeping a reasonable dimension of the restricted Hilbert space. We investigated how referred results change with the number of considered levels. The table informs about our result for $\lambda = 0.05$

q	4	6	8	10	12	15	20
$\text{Re } \eta_0 \times 10^{+16}$	-6.301 54	-0.666 20	0.063 80	-1.491 58	3.607 22	12.267 76	-0.197 85
$\text{Re } \eta_1 \times 10^{+9}$	-2.835 37	-1.711 37	-1.256 71	-1.130 70	-1.102 06	-1.095 55	-1.095 01
$\ln[-\text{Re } \eta_1]$	-19.681 10	-20.185 97	-20.494 77	-20.600 43	-20.626 08	-20.632 01	-20.632 50

and for $\lambda = 1.0$,

q	4	6	8	10	12	15	20
$\text{Re } \eta_0 \times 10^{+14}$	-15.672 15	3.392 38	0.904 57	9.732 75	-1.196 53	-2.072 02	19.627 54
$\text{Re } \eta_1 \times 10^{+2}$	-3.135 85	-3.2182	-3.230 45	-3.232 08	-3.232 25	-3.232 26	-3.2326
$\ln[-\text{Re } \eta_1]$	-3.462 27	-3.436 34	-3.432 55	-3.432 04	-3.431 99	-3.431 99	-3.431 99

The restriction to the vacuum and the first ten excited levels revealed to be sufficient for our calculation and such a number is also computationally available. However, the appropriate number q depends on parameters of the model, mainly on the chosen polaron shift γ (connected with the distortion of levels) and also on the temperature (connected with the occupation of higher states). We conclude that errors of the referred results, coming from the numerical implementation, can hardly be the source of doubts. At the end, we note that the observed exponent $k = 6$ in (10) is not sensitive to the change of the parameters and that this value was observed for a wide range of parameters.

Appendix B. Another type of scaling

Another type of scaling could also be the subject of the above arguments. Our choice of what should be the perturbational parameter in the Hamiltonian should be in accordance with the typical physical situation and the regime we have in mind. We refer the result for the same Hamiltonian (in $\lambda = 1$), but with another proportionality to the perturbational parameter λ of what is to be considered as a perturbation in the total Hamiltonian H . Specifically

$$H_S = \lambda \hbar J (c_0^\dagger c_1 + c_1^\dagger c_0)(b + b^\dagger) + \hbar \epsilon c_1^\dagger c_1 + \hbar \omega (b^\dagger + \gamma c_0^\dagger c_0)(b + \gamma c_0^\dagger c_0).$$

Such a scaling coincides with the Davies one from [4], if we interpret $[J, \dots]$ as a λ proportional generator of the Davies semigroup. The behaviour of the system can in principle entirely differ, in connection with another regime to which our new choice corresponds. However, we arrive at the conclusion that the result obtained above does not change in any dramatic way if our interest is focused on general features of the asymptotics. The only change in Tokuyama–Mori coefficients (3) in the second order is that term in \mathcal{L}^c proportional to J is now proportional to λ instead of λ^2 . Some changes, however, arise in the power series of the asymptotic density matrix treated according to subsection 3.B. We refer results here, further consequences are parallel to the previous scaling:

$$\begin{aligned} \rho(t = \infty) &= \sum_{i=0}^{\infty} \lambda^i \rho^{(i)} \\ i \neq j \quad \rho_{i,j}^{(0)} &= 0 \\ \rho_{\alpha\alpha,\alpha\alpha}^{(0)} &= C_\alpha \exp[-\hbar\alpha\omega\beta_T] \\ \rho_{\alpha\alpha,\alpha\beta}^{(1)} &= 0 \quad \alpha \neq \beta \\ \rho_{0\alpha,1\beta}^{(1)} &= J[\sqrt{\beta}\langle\alpha'|\beta-1\rangle + \sqrt{\beta+1}\langle\alpha'|\beta+1\rangle] \frac{C_0 e^{-\hbar\alpha\beta_T\omega} - C_1 e^{-\hbar\beta\beta_T\omega}}{\omega(\alpha-\beta) - \epsilon}. \end{aligned}$$

For $\mu \neq \nu$ we obtain these second order results:

$$\begin{aligned} \rho_{1\mu,1\nu}^{(2)} &= \frac{J^2}{\omega(\mu-\nu)} \sum_{\alpha=0}^{\infty} \langle\mu|b+b^\dagger|\alpha'\rangle \langle\alpha'|b+b^\dagger|\nu\rangle \\ &\quad \times \left[\frac{C_0 e^{-\hbar\alpha\beta_T\omega} - C_1 e^{-\hbar\mu\beta_T\omega}}{\omega(\alpha-\mu) - \epsilon} - \frac{C_0 e^{\hbar\alpha\beta_T\omega} - C_1 e^{-\hbar\nu\beta_T\omega}}{\omega(\alpha-\nu) - \epsilon} \right] \\ \rho_{0\mu,0\nu}^{(2)} &= \frac{J^2}{\omega(\mu-\nu)} \sum_{\alpha=0}^{\infty} \langle\mu'|b+b^\dagger|\alpha\rangle \langle\alpha|b+b^\dagger|\nu'\rangle \\ &\quad \times \left[\frac{C_0 e^{\hbar\mu\beta_T\omega} - C_1 e^{-\hbar\alpha\beta_T\omega}}{\omega(\mu-\alpha) - \epsilon} - \frac{C_0 e^{-\hbar\nu\beta_T\omega} - C_1 e^{-\hbar\alpha\beta_T\omega}}{\omega(\nu-\alpha) - \epsilon} \right] \end{aligned}$$

and the following condition for $\rho_{0\mu,1\nu}^{(2)}$

$$\rho_{0\mu,1\nu}^{(2)} = \frac{J \langle\mu'|b+b^\dagger|\nu\rangle [\rho_{0\mu,0\mu}^{(1)} - \rho_{1\nu,1\nu}^{(1)}]}{\omega(\mu-\nu) - \epsilon}.$$

We mention here that $\rho_{av,av}^{(1)}$ are to be understood as arbitrary parameters. The coefficients that we have not mentioned cannot be specified better in our machinery.

References

- [1] Davies E B 1976 *Quantum Theory of Open Systems* (London: Academic)
- [2] Čápek V and Mančal T 1999 *Europhys. Lett.* **48** 365
- [3] Čápek V and Bok J 2001 *Physica A* **290** 379
- [4] Davies E B 1976 *Math. Ann.* **219** 147
- [5] Davies E B 1974 *Commun. Math. Phys.* **39** 91
- [6] van Hove L 1955 *Physica* **21** 517
van Hove L 1957 *Physica* **23** 441
- [7] Čápek V and Barvík I 2001 *Physica A* **294** 388
- [8] Čápek V 2002 *Eur. Phys. J. B* **25** 101
- [9] Alicki R and Lendi K 1987 *Quantum Dynamical Semigroups and Applications (Lecture Notes in Physics vol 286)* (Berlin: Springer)
- [10] Gorini V, Frigerio A, Verri M, Kossakowski A and Sudarshan G 1978 *Rep. Math. Phys.* **13** 149
- [11] Davydov A S 1973 *Kvantovaja Mehanika* (Moscow: Nauka) (in Russian) (German Translation of the 5th edn: Dawydow A S 1978 *Quanten Mechanik* (Berlin: VEB Deutscher Verlag der Wissenschaften))
- [12] Bogolyubov N N 1946 *ZETP* **16** 8
- [13] Akhiezer A I and Peletminskii S V 1977 *Methods of Statistical Physics* (Moscow: Nauka) (in Russian)
- [14] Reed M and Simon B 1978 *Methods of Modern Mathematical Physics: IV. Analysis of Operators* (New York: Academic) p 21, theorem XII.11
- [15] Kato T 1966 *Perturbation Theory for Linear Operators* (Berlin: Springer) (2nd edn 1976)
- [16] Čápek V and Bok J 2002 *Chem. Phys.* **277** 101
- [17] May V and Kühn O 2000 *Charge and Energy Transfer Dynamics in Molecular System* (Berlin: Wiley-VCH Verlag)
- [18] Čápek V 1994 *Physica A* **203** 495
- [19] Peřina Jr J 1995 *Physica A* **214** 309
- [20] Nakajima S 1958 *Prog. Theor. Phys.* **20** 948
- [21] Zwanzig R 1964 *Physica* **30** 1109
- [22] Fuliński A and Kramarczyk W J 1968 *Physica* **39** 575
- [23] Tokuyama M and Mori H 1976 *Prog. Theor. Phys.* **55** 411
- [24] Landau L D and Teller E 1936 *Phys. Z. Sowjetunion* **10** 34
- [25] MacLane S and Birkhoff G 1968 *Algebra* (New York: Macmillan)
- [26] Smith B T, Boyle J M, Dongarra J J, Garbow B S, Ikebe Y, Klema V C and Moler C B 1976 *Matrix Eigensystem Routines—EISPACK Guide* (New York: Springer)