On a naive construction of kinetic equation

F. Šanda

Institute of Physics of Charles University,
Faculty of Mathematics and Physics,
Ke Karlovu 5, 121 16 Prague 2, Czech Republic
(Tel. (**-420-2)2191-1341, Fax (**-420-2)2492-2797, E-mail sanda@karlov.mff.cuni.cz)

(Dated: February 17, 2022)

Abstract

We return to the subject of stability of infinite time asymptotics of kinetic equations. We found a model which is simpler than those studied previously and which shows unstable behavior corresponding to our arguments from [1], where, however, a relatively complicated problem was treated. Our simplification to four levels interacting with surroundings enable us to proceed easily through all the way with just a pen and paper. We provide no numerical modelling whose justification causes naturally difficulties to the reader. We draw also further consequences of the found instability, not only with respect to higher order terms in kinetic equations but also concerning the very philosophy of physical modelling. The latter point can give more practically oriented physicist even better motivation than mere speculations about potential instabilities due to higher order terms in perturbation treatments without concrete resolution of correct asymptotics.

PACS numbers: 05.30.-d,03.65.Ca

Keywords: Kinetic equations
I. INTRODUCTION

Subject of our paper are new results questioning stability of solution of kinetic equations. Kinetic equations are widely used in solid state or statistical physics in modelling of transfer processes including relaxation phenomena, influence of external fields etc. This concerns a great number of physical theories appropriate for different physical regimes of interest like Boltzmann equation [2], Fokker-Planck equation [3], Pauli master equation [4], or its generalized version introduced independently in different forms by Zwanzig, Mori [5, 6] etc. General mathematical structure of these theories is the set of differential or integro-differential equations (of the first order), which determine time evolution of quantities of interest. Specific type of these differential equations is not unique, in its easiest form we meet with time independent Markov process (without memory), the other may contain time dependencies in coefficients (for example dependence on external fields), memory terms (time nonlocal equations), or inhomogenous terms or nonlinearity. Instabilities or chaotic behavior in case of complicated nonlinear equations are surely not very surprising. Below we will deal with the easiest form of such equations - the set of linear differential equations with constant coefficients. Specific topic of this work is scrutiny of stability of steady state, including that of the attractor nature of the steady state. Let us give some comments here, how this treatment is related to the other types of mathematical structure which are also used in physically similar treatments, and about physical consequences of this work. Time-local and memory-including theory of Markov processes are related in general (for general mathematical theory- see for example [7]) and also explicit equivalence for specific type of equations stemming from the Liouville equation could be found [8]. The goal of this work is to argue that memory for Markov processes can be integrated into time local coefficients. In addition we are interested in steady state and infinite time asymptotics. Coefficients (in evolution matrix) often turn into time independent ones in infinite time region [9, 10]. Some kind of Markov approximation here becomes exact. This provides the connection with our work. Influence of external fields is further property which can be often related with topic of our interest.

The origin of kinetic equations is mostly in perturbational theories, which turn fundamental microscopical physical laws into differential equations determining time evolution of macroscopic quantities available in experiments. For practical purposes the coefficients are
usually approximated by calculation of leading terms of the Taylor series in a perturbational parameter. Quite usual is using approximation of the second order in coupling to uncontrolled degrees of freedom, what enables to incorporate connected relaxation phenomena.

Then the time evolution of ”quantities of physical interest” is solved. Formally, validity of all these approximations of the perturbational origin is limited on the time axis. On the other hand, these are the steady state and asymptotic limit which are of the greatest physical importance. Otherwise well applicable theory is thus asked to achieve reasonable results also for this time region. Expected results like the Boltzmann distribution were found in the simplest kinetic models, what gave physicists strong belief in general applicability of the particular kinetic theory. There is a statement that little changes of coefficients can not change in very dramatic way results of numerical studies, which is usually considered as ”physically reasonable” . However, we want to argue that this statement is NOT true.

Recently we found in [1] rather unexpected instability in asymptotical behavior in case of a not very complicated open system. The latter showed some not very standard features, but no direct indication of internal collapse in modelling of time development, of the type of, e.g., a clearly unphysical result. Many model approximations, where one can meet the below described instability, may seem to be quite usual or not very suspicious.

However, whatever is the truth about correct time asymptotics of the model hamiltonian from [1], we would like to warn the reader against unexpected features encountered in this problem. When one incorporates (according to his/her opinion) important physical processes into kinetic equations, attention must be also focused on stability of the solution of the problem. In particular the question is which part of the results is correct and which is only a belief (and contingently only an unjustified belief). In case when the resulted steady state can not be confronted with, e.g., thermodynamical laws, the result of thus invalid simulation may seem to be quite good.

Sometimes physical belief in the second order approximation results is hidden into sophisticated mathematical methods which pretend to give a ”general” proof of correctness of the second order results without realistic treatment of the stability, case by case. Such methods might, regardless of their mathematical validity and usefulness, in concrete appli-
cations leave a space for speculations about existence of instabilities, in some important 
features of the solution, like in our model from [1]. In [1] we showed how it is possible to 
fulfil so called Davies theorems [11] and, simultaneously, also obtain sharp instability in the 
long time regime behavior against higher order contributions to Tokuyama-Mori coefficients. 
The proper quantity of our interest is time asymptotics of the kinetic equation (regardless 
of whether the steady state is given only by internal dynamics, or it is influenced by some 
regular external field, presence of interchange particle etc.).

Organization of our paper is the following: In part 2 we introduce a quite usual transfer 
process model - four site open quantum system interacting with surroundings. We perform 
standard treatment using second order perturbational theory of relaxation with full spectral 
analysis of evolution matrix and the unique asymptotic steady state will be found. One can 
verify that the model, at least in standard thinking, contains description of all the important 
physical processes present here. Further we introduce (in section 3) a correction to evolution 
matrix. We thus add a transfer channel, whose description is constructed in the same way 
like that of the previous ones. However, we assume the effectiveness of the new channel to 
be very small with respect to that of the original channels. This new process is also not 
apparently seen to change overall properties of system. Nevertheless, dramatic changes in 
the steady state will appear. The small perturbation will be treated in two distinct ways. 
First we consider it like a higher order correction in the perturbation series to our second 
order approximation. This approach is in our view mathematically more interesting, but is 
rather speculative because we do not explicitly calculate all the fourth order contribution 
that can come from higher order calculation in some exact microscopical theory. However, 
the instability of the second order approximation is verified regardless this objection. The 
second possibility is to complement the model by a further small parameter which will be 
limited to zero after the asymptotic calculation. In this case we fully stay at a position of the 
standard second order kinetic theory, but we consider model character of our hamiltonian 
as in the everyday physics, and we treat stability of the model conclusions against ”omitted 
physically irrelevant” process. In part 4 we throw some light on indication of instability of 
the given type. At first we show its indication in spectrum of the evolution matrix, then 
a purely analytical treatment of stability will be given. In part 5 we compare our result 
with van Hove limit of the same model Hamiltonian. We will find a connection with some 
pathological case of this well understood limit, where kinetic theory also may have problems
with establishing of asymptotical state.

All these ideas are presented on this simple model. Further consequences about relation to Davies theorems are not repeated, interested reader can find them in [1]. All the calculations are hand made product and the reader is pretty invited to follow them. The reader is also invited to think how the referred problems, which one may consider as clear or quite trivial, may become forgotten when a complicated model is treated which is not analytically calculable, but where only computer simulations are at hand.

II. MODEL

Let us consider the following model hamiltonian of a four site open system. We measure energy in units $\bar{\hbar}$.

$$H = \epsilon (c_1^{\dagger}c_1 + c_3^{\dagger}c_3) + J (c_2^{\dagger}c_3 + c_3^{\dagger}c_2) + \sum_k \{ G_k^{(1-2)} (B_k c_1^{\dagger} c_2 + B_k^{\dagger} c_2^{\dagger} c_1) + G_k^{(3-4)} (B_k c_3^{\dagger} c_4 + B_k^{\dagger} c_4^{\dagger} c_3) + \Omega_k B_k^{\dagger} B_k \}$$

(1)

This hamiltonian describes our four site system where creation $c_i^{\dagger}$ and annihilation operators $c_i$ are each related to the i-th site, with three transfer channels, two of them being bath-induced the remaining one being coherent. As far as we consider one particle only, there is no necessity to introduce (anti)commutational relations between these operators. Dynamics of the system is dominated by bath induced transfer channels between 1-2 and 3-4 sites and a coherent transfer channel 2-3. $B_k^{\dagger}, B_k$ are creation and annihilation operators of k-th bath phonon mode (fulfilling boson commutational relation), $G_k^{(i-j)}$ are coupling constants of the system-bath interaction. Parameter J describes power of the coherent channel.

We do not allow the interference between bath induced channels 1-2 and 3-4, what means to fulfil conditions like:

$$\sum_k \delta(\epsilon - \Omega_k) G_k^{(1-2)*} G_k^{(3-4)} Tr_{Bath}(\rho_{Bath} B_k^{\dagger} B_k) = 0.$$  

This can be generally fulfilled if one considers that the particular transfer channels are induced by different phonon modes

$$G_k^{(1-2)} G_k^{(3-4)} = 0.$$  

One can treat this hamiltonian using various schemes. Firstly, it is possible to think about different regimes, according to different magnitude of the coefficients in Hamiltonian.
We are here interested in the regime where it is appropriate to treat J- and bath-induced transfer channel as a perturbation. We emphasize that this choice does not correspond to so-called van Hove limit \[12\]. One can diversify the physical interpretation of hamiltonian (1) and a chosen perturbation scheme. Coherent channel one can consider as a slow internal motion treated according to \[13\], but it may also represent constant or periodical external field influence.

Various constructions of kinetic equations can be also applied. We restrict ourselves to those which respect chosen mathematical structure and the physical regime. Though also here physicist use various formalisms, one may obtain our results using Nakajima-Zwanzig identity, Tokuyama-Mori equation (both in their second order approximation), and also Haken-Strobl-Reineker parameterization \[14, 15\]; all these ways lead to formally the same master equation:

\[
\frac{d\rho_{ij}}{dt} = \sum_{\{kl\}} W_{\{ij\},\{kl\}} \rho_{\{kl\}} \tag{2}
\]

where vector $\rho$ is organized in the following way

\[
\rho^T = (\rho_{11}, \rho_{22}, \rho_{33}, \rho_{44}, \text{Re}\rho_{23}, \text{Im}\rho_{23}, \text{Re}\rho_{12}, \text{Im}\rho_{12}, \text{Re}\rho_{13}, \text{Im}\rho_{13}, \text{Re}\rho_{34}, \text{Im}\rho_{34}, \text{Re}\rho_{24}, \text{Im}\rho_{24}, \text{Re}\rho_{14}, \text{Im}\rho_{14})
\]

Matrix $W$ we call evolution matrix. $W^{(2)}$ is the second order approximation of $W$. It reads

\[
W^{(2)} = \begin{pmatrix}
A & 0 & 0 & 0 \\
0 & B & 0 & 0 \\
0 & 0 & C & 0 \\
0 & 0 & 0 & D
\end{pmatrix}
\]

where

\[
A = \begin{pmatrix}
-\Gamma_\downarrow & \Gamma_\uparrow & 0 & 0 & 0 & 0 \\
\Gamma_\downarrow & -\Gamma_\uparrow & 0 & 0 & 0 & -2J \\
0 & 0 & -\Gamma_\downarrow & \Gamma_\uparrow & 0 & 2J \\
0 & 0 & \Gamma_\downarrow & -\Gamma_\uparrow & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\Gamma_\uparrow + \Gamma_\downarrow}{2} & -\epsilon \\
0 & J & -J & 0 & \epsilon & -\frac{\Gamma_\uparrow + \Gamma_\downarrow}{2}
\end{pmatrix}
\]
\[
B = \begin{pmatrix}
\frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} & \epsilon & 0 & -J \\
-\epsilon & \frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} & J & 0 \\
0 & -J & -\Gamma_\downarrow & 0 \\
J & 0 & 0 & -\Gamma_\downarrow \\
\end{pmatrix},
\]
(5)
\[
C = \begin{pmatrix}
\frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} & \epsilon & 0 & J \\
-\epsilon & \frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} & -J & 0 \\
0 & J & -\Gamma_\uparrow & 0 \\
-J & 0 & 0 & -\Gamma_\uparrow \\
\end{pmatrix},
\]
(6)
\[
D = \begin{pmatrix}
\frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} & \epsilon \\
-\epsilon & \frac{-\Gamma_\uparrow + \Gamma_\downarrow}{2} \\
\end{pmatrix},
\]
(7)
Here
\[
\Gamma_\uparrow = 2\pi \sum_k [G_k^{\text{1-2}}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{Bath}} \rho_{\text{Bath}}(B_k^\dagger B_k) = 2\pi \sum_k [G_k^{\text{3-4}}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{Bath}} (\rho_{\text{Bath}} B_k^\dagger B_k) \\
\Gamma_\downarrow = 2\pi \sum_k [G_k^{\text{1-2}}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{Bath}} (\rho_{\text{Bath}} B_k B_k^\dagger) = 2\pi \sum_k [G_k^{\text{3-4}}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{Bath}} (\rho_{\text{Bath}} B_k B_k^\dagger).
\]
(8)
The equality of coefficients for 1-2 and 3-4 transfer is our additional assumption, that cannot be deduced from (1). Notice that \(J, \Gamma_\uparrow, \Gamma_\downarrow\) we consider as perturbations of the same magnitude, proportional to the parameter \(\lambda^2\).
\[
J, \Gamma_\uparrow, \Gamma_\downarrow \propto \lambda^2
\]
(9)
(Reason the proportionality is only a consistency with standard perturbational order of bath-induced transfer channel.)

The steady state is given by the condition:
\[
\sum_{\{kl\}} W_{\{ij\},\{kl\}} \rho_{\{kl\}} = 0
\]
(10)
We are now to calculate the complete spectrum of the evolution matrix. Firstly: this enables us to show that steady state is also the unique asymptotic state of this equation. Furthermore we will argue that the solution has no apparent deviant feature. Last but not least, in section 4 we will show that in a careful treatment one can indicate, in this spectrum, the instability calculated below.
The evolution matrix was arranged so that it has a quasidiagonal structure. We have to calculate a characteristic equation. After bit of algebra (we must calculate determinant of submatrices of maximal order 6) and rearranging resulting terms, we obtain:

\[ 0 = \xi \cdot (\xi + \Gamma \uparrow + \Gamma \downarrow) \cdot \{\xi(\xi + \Gamma \uparrow + \Gamma \downarrow)[(\xi + \frac{\Gamma \uparrow + \Gamma \downarrow}{2})^2 + \epsilon^2] + 4J^2(\xi + \frac{\Gamma \uparrow + \Gamma \downarrow}{2})^2\} \]

\[ \cdot \{\xi + i\epsilon + \frac{\Gamma \uparrow + \Gamma \downarrow}{2})(\xi + \Gamma \downarrow) + J^2\} \cdot \{\xi - i\epsilon + \frac{\Gamma \uparrow + \Gamma \downarrow}{2})(\xi + \Gamma \downarrow) + J^2\} \]

\[ \cdot \{(\xi + \Gamma \uparrow + \Gamma \downarrow)^2 + \epsilon^2\} \quad (11) \]

Twelve roots can be calculated directly from the quadratic terms. What remains is an equation of the fourth order. The roots can be in principe also extracted using Cardano formula, but it does not provide an easy survey. Instead we inspect behavior in the \( \lambda \rightarrow 0 \) limit of the perturbational parameter. This analysis and calculation of twelve exact eigenvectors is provided in Appendix.

In conclusion: there is only one steady state and, at least for not very high parameter \( \lambda \), all the other eigenvectors of matrix \( \mathbf{3} \) have negative real parts, i.e. connected terms in time evolution simulation disappear in the infinite time and the steady state is also the asymptotical one. Because of finite order of the matrix there is a region surrounding the zero, where this problem has infinite time asymptotics given by (11), so one can limit himself/herself to this region without complications. For very high values of \( \lambda \) parameter, the model need not have the correct behavior in accordance with general inapplicability of the perturbational treatment for this case. The worth notice is that the zero eigenvalue came purely from the first submatrix \( \mathbf{A} \). The others have nonzero determinants and thus the only solution of the steady state condition must be zero for associated elements in the density matrix.

We can give at this place the solution to steady state condition (11). We work with normalization condition

\[ \sum_i \rho_{ii} = 1. \quad (12) \]

---

1 The terms are ordered according to ordering of submatrices; one submatrix is one row.
Then the result is:

\[ \rho_{11} = \frac{\Gamma_\uparrow^2}{(\Gamma_\uparrow + \Gamma_\downarrow)^2}; \quad \rho_{22} = \rho_{33} = \frac{\Gamma_\uparrow \Gamma_\downarrow}{(\Gamma_\uparrow + \Gamma_\downarrow)^2}; \quad \rho_{44} = \frac{\Gamma_\downarrow^2}{(\Gamma_\uparrow + \Gamma_\downarrow)^2}; \quad \rho_{i\neq j} = 0. \] (13)

We specifically note the equality in population at sites 2 and 3. The reader may speculate whether this model and result are in whatever sense bad. In any case, there is no internal collapse in these calculations. One may be suspicious about the fact that the model does not lead to thermodynamical equilibrium, but as we notice above we do not argue that this system is in thermodynamical equilibrium as we are not in the van Hove limit, and also the purely internal character of the coherent transfer was not specified. There are some physicists who believe that the validity of thermodynamical laws must be in some direction connected with the van Hove limit [16]. The 2-3 channel is elastic what implies 2-3 symmetry and consequent equality \( \rho_{22} = \rho_{33} \). The transfer term proportional to \( J \) can come also from defined (e.g. harmonic) external field; then thermodynamical prediction can fail or this prediction need not be clear without further calculations.

### III. PERTURBATION

In this section we introduce a small perturbation of model (1) in form of an incoherent transfer channel between sites 2 and 3. The new terms in evolution matrix can be quite small with respect to the other ones coming from the previous consideration. Construction of the terms is fully analogical to the previous one. Formally one can include a change into hamiltonian:

\[ \delta H = \sum_k G_k^{(2-3)}(B_k c_3^\dagger c_2 + B_k^\dagger c_2^\dagger c_3). \]

We refer a new corrected evolution matrix, the effectiveness of the new 2-3 channel is measured by rate coefficients \( g_\uparrow, g_\downarrow \):

\[ A = \begin{pmatrix}
-\Gamma_\downarrow & \Gamma_\uparrow & 0 & 0 & 0 & 0 \\
\Gamma_\downarrow & -\Gamma_\uparrow - g_\uparrow & g_\downarrow & 0 & 0 & -2J \\
0 & g_\uparrow & -\Gamma_\downarrow - g_\downarrow & \Gamma_\uparrow & 0 & 2J \\
0 & 0 & \Gamma_\downarrow & -\Gamma_\uparrow & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\Gamma_\uparrow + \Gamma_\downarrow + g_\uparrow + g_\downarrow}{2} & -\epsilon \\
0 & J & -J & 0 & \epsilon & -\frac{\Gamma_\uparrow + \Gamma_\downarrow + g_\uparrow + g_\downarrow}{2}
\end{pmatrix}, \] (14)
The term "small perturbation" has to be formalized in order to talk about the instability. We have worked out this point in two different ways. First of them is submitted mainly for a mathematically oriented reader. We consider \( g_\uparrow, g_\downarrow \) as proportional to \( \lambda^4 \).

\[
J, \Gamma_\downarrow, \Gamma_\uparrow \propto \lambda^2 \quad g_\uparrow, g_\downarrow \propto \lambda^4
\]
One may have some physical objections against this interpretation, stemming from the fact, that we did not provide complete 4-th order inspection of the kinetic theory. But we have quite narrow ambition here. We point out the instability of the result (13) against the 4-th order correction, which we consider to be arbitrary - as a potentiality. We argue that an arbitrary perturbation could be used to achieve this conclusion. The physical motivation in this interpretation is in the background only, in order to get the reader interested, the statement is of mathematical character. One can also omit here the additional term in Hamiltonian $\delta H$, and think of the perturbation as of a higher order terms coming potentially from the Hamiltonian (1) that are omitted in standard second order calculation. We will compare the results (13) and (16) in $\lambda \to 0$ limit where the perturbational treatment is best verified. (Performing this limit has of course no consequence in connection with the main statement - instability.)

The second interpretation stays fully on the position of the second order kinetic equation. We introduce some further parameter $\eta$ that measures relative power of different transfer channel

$$J, \Gamma_\downarrow, \Gamma_\uparrow \propto \lambda^2 \quad g_\uparrow, g_\downarrow \propto \eta \lambda^2. \quad (19)$$

After evaluation of the $\lambda \to 0$ limit, which gives precise mathematical sense to our calculation, we consider $\eta$ to be small, formally limiting to 0. We shall show that regardless the arbitrarily small (but nonzero) magnitude of $\eta$, the result (13) is not preserved. In other words,

$$\lim_{\eta \to 0} \rho(\eta) \neq \rho(\eta = 0)$$

$\rho$ designates here the steady state in $\lambda \to 0$ limit. This is the central statement that we are going to prove. We inspect the stability of standard kinetic equations with respect to physical processes which were not incorporated into a model in question because of their not high strength (at least from a formal, cursory point of view) and consequent underestimating their influence. This point is possibly not so interesting mathematically because the second order theory is held here, but it seriously questions the straightforward applicability of the standard kinetics from the physical point of view. Both these interpretations are from mathematical and also from physical context quite distinct. We argue that the instable behavior is the internal problem of the approximation (3) and does not come from the very specialized choice of perturbation or scheme of its treatment. In the next subsection we
make this point more clear.

Performing the announced limits:

First interpretation (18):

$$\lim_{\lambda \to 0} \rho_{22} = \lim_{\lambda \to 0} \rho_{33} = \frac{\lambda^4 g \left( \frac{2\epsilon^2}{2\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow) + \lambda^4 (\delta \uparrow + \delta \downarrow)} + \frac{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow + \eta(\delta \uparrow + \delta \downarrow))}{2} \right)}{\lambda^4 g \left( \frac{2\epsilon^2}{2\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow) + \lambda^4 (\delta \uparrow + \delta \downarrow)} + \frac{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow + \eta(\delta \uparrow + \delta \downarrow))}{2} \right)} + 2\lambda^4 J^2 = \frac{g_\downarrow}{g_\uparrow}$$

Second interpretation (19):

$$\lim_{\eta \to 0} \lim_{\lambda \to 0} \rho_{22} = \lim_{\eta \to 0} \lim_{\lambda \to 0} \rho_{33} = \frac{\eta \lambda^2 g \left( \frac{2\epsilon^2}{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow) + \eta(\delta \uparrow + \delta \downarrow)} + \frac{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow + \eta(\delta \uparrow + \delta \downarrow))}{2} \right)}{\eta \lambda^2 g \left( \frac{2\epsilon^2}{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow) + \eta(\delta \uparrow + \delta \downarrow)} + \frac{\lambda^2 (\Gamma_\uparrow + \Gamma_\downarrow + \eta(\delta \uparrow + \delta \downarrow))}{2} \right)} + 2\lambda^4 J^2 = \lim_{\eta \to 0} \frac{g_\downarrow}{g_\uparrow} = \frac{g_\downarrow}{g_\uparrow}$$

Also other results are identical in both our limits, we refer it in a short way.

\[
\begin{align*}
\rho_{11} &= \frac{\Gamma_\uparrow^2 g_\downarrow}{(\Gamma_\uparrow + \Gamma_\downarrow)(\Gamma_\downarrow g_\downarrow + \Gamma_\uparrow g_\uparrow)} \\
\rho_{22} &= \frac{\Gamma_\downarrow \Gamma_\uparrow g_\downarrow}{(\Gamma_\uparrow + \Gamma_\downarrow)(\Gamma_\uparrow g_\downarrow + \Gamma_\downarrow g_\uparrow)} \\
\rho_{33} &= \frac{\Gamma_\downarrow \Gamma_\uparrow g_\uparrow}{(\Gamma_\uparrow + \Gamma_\downarrow)(\Gamma_\uparrow g_\downarrow + \Gamma_\downarrow g_\uparrow)} \\
\rho_{44} &= \frac{\Gamma_\downarrow^2 g_\uparrow}{(\Gamma_\uparrow + \Gamma_\downarrow)(\Gamma_\uparrow g_\downarrow + \Gamma_\downarrow g_\uparrow)} \\
Re \rho_{23} &= 0; \quad Im \rho_{23} = 0 \quad (20)
\end{align*}
\]

We clearly see that if \( g_\uparrow \neq g_\downarrow \), then sharp changes appear in solution (13). We did not assume equality between these coefficients. Moreover the physical motivation of our correction points out to \( g_\uparrow \neq g_\downarrow \). Rather the standard thermodynamics relation

\[
\frac{g_\uparrow}{g_\downarrow} = \exp \beta \epsilon
\]

may be assumed. Derivation of this statement consists in some additional assumptions about initial state of the bath, which are, however, standard. Of course, if one is interested in the Taylor series structure in higher order expansion of (17), our interpretations are mutually different, but the general picture is not changed.

We would like to give further warning here. One need not be very surprised because of the following argumentation. Transfer channel connected with parameter J is in fact physically also of the fourth order, because its direct application to density matrix (commutator \([J, \rho]\) ) change either the ket or bra side of density matrix only and comparable process connecting
the diagonal terms in density matrix is thus of the fourth order. Then this new included channel is comparably strong (in the first interpretation) or even stronger (in the second argumentation) than the first one. We give threefold counterargument:

1, - Nevertheless, formally the coherent process (J-proportional) is included in the second order. Such a treatment is absolutely standard. Care in this direction becomes difficult or technically unable for complicated system. Moreover this objection also seriously questions concept of the generalized master equation in general, because treatment of the whole density matrix (of the system) included information about set of generally incompatible observables. With respect to a particular measurement (here for example site probability measurements) the other terms unrelated to this measurement (here off-diagonal matrix element) have always the role of some kind of memory. So their treatment apparently differs from that of bath induced channel one.

2, - Physical intuition in more complicated case is uncertain and may fail.

3, - If one is internally sure about his/her intuition, please try inspect the formula (17) again now with the following scheme

\[
\Gamma_\uparrow, \Gamma_\downarrow, J \propto \lambda^2; \quad g_\uparrow, g_\downarrow \propto \lambda^5
\]

or alternatively

\[
\Gamma_\uparrow, \Gamma_\downarrow, J \propto \lambda^2 \quad g_\uparrow, g_\downarrow \propto \eta \lambda^4.
\]

One can see here that in the same limits as above, the instability is still present, though the perturbation should be now smaller than the fourth order coherent channel. In fact the coherent channel transfer is seemingly of the higher order then 4! Have you seen it before this limit calculation?

IV. INDICATION OF INSTABILITY

We have argued in the previous section, that instability described above is the matter of internal problem of approximation \([4]\). Despite of its reasonable behavior in time evolution simulation which we proved in Appendix, a problematic step has been indicated above and this problem must be visible purely from the second order approximation calculation. In
fact, if one were not able to give some indication of the instability of the approximation from itself, the situation would have been critical. At first: Calculation in higher order is not standard, and what is worse, it is an extremely difficult task. The second problem is that in that case one can never (in no finite order of calculation) be sure whether the provided approximation is already stable. We give two points which are connected with our instability and indicate it.

A. Long-time excitation in the spectrum

This method enables us to show quite simply how to obtain the indication purely from spectrum of the evolution matrix in the second order approximation. What is important from practical point of view, one may use this method without principal difficulties also in complicated models by numerical analysis and, further, may in many ways also implement orientational indication into her/his time evolution computer simulation. Only for simplicity and without any change in physical context we assume that the number of linearly independent eigenvectors equals to the order of the matrix. In problem (3) this statement is proven, because none of the submatrix has two identical eigenvalue. The general form of spectral decomposition of finite (non-normal) matrix is then:

\[ W_{ij} = \sum_q \xi_q(L_q)_i(R_q)_j \]

where \( \xi_q \) is q-th eigenvalue and \( R_q(L_q) \) is the associated right(left i.e usual) row (column) eigenvector. This decomposition holds good this normalization:

\[ \sum_i (R_q)_i(L_q')_i = \delta_{qq'} \]

Kinetic equations conserve total probability, what results into the fact that eigenvalue 0 is always present. Have a look at our result in the Appendix again. The very suspicious eigenvalue is \( \xi_4 \). In perturbation scheme (9), there is a proportionality \( \xi_4 \propto \lambda^6 \). No wonder that this eigenvalue need not be very stable against our perturbation regardless of the type of scheme. More generally: Let us have, in our spectrum, eigenvalue with real part approaching zero (with \( \lambda \to 0 \)) and proportional to higher than second power of \( \lambda \) (\( n > 2 \)):

\[ W_{ij} = 0 \cdot (L_0)_i(R_0)_j + a_1 \lambda^n \cdot (L_1)_i(R_1)_j + \ldots \]
We explicitly emphasize that also \((L_q), (R_q)\) are \(\lambda\)-dependent what only enables that \(W_{ij}\) has terms of just the second order.

Then one can easily construct the mathematical ”perturbation” which causes the instability, for example perturbation

\[
\delta W_{ij} = -\lambda^n \cdot (L_0)_i (R_0)_j - a_1 \lambda^n \cdot (L_1)_i (R_1)_j + \mathcal{O}(\lambda^n)
\]

that change the stationary state from \((L_0)\) to \((L_1)\) in the limit.

In the first perturbational technique \((18)\) possibility of such construction is straightforward. In the second case \((19)\) we must construct it from the more complicated terms, but one can see in our model \((16)\) that it is possible. Of course, not each one of the mathematical ”perturbations” is physically interpretable. One usually has some conditions for the evolution matrix stemming from the conservation laws (at least particle conservation in case of solid state physics), etc., but the set of possible perturbations is so great, that it surely contains also reasonable perturbations. One of them we introduced in subsection 3. In our problem, there is the ”near-the-zero” eigenvalue proportional to the sixth order in \(\lambda\), so we could choose the perturbation smaller than we have done. Concluding this subsection we notice that the reciprocal real part of eigenvalue (without sign) can be also called the lifetime of ”excitation” (though it need not be a very appropriate name in some cases). This provides practical indication of this instability - highly increasing lifetime of relaxation phenomena when the parameter of perturbation is reduced according to formal scheme of construction of given kinetic equation. Because of clarity of this point we do not give any formal statement.

**B. Analytical treatment of stationary condition**

In this subsection we give an easy example of analytical stationary condition \((10)\) treatment. This treatment is stable against perturbation. We know that it need not be usually the very appropriate method from practical point of view. When a direct explicit resolution is not available (for more complicated or extended problems) one must take extreme care in computational implementation about numerical errors. The main reason for introducing this calculation is further understanding of the origin of the instability for the reader who still has not internally accepted the presented facts. For our treatment we need (for simplicity)
to assume that there is a unique asymptotical state of the system. This is because we will
here take care of the stability of the zero eigenvector of the evolution matrix only. This
treatment does not provide the proof that there is no potential eigenvalue with positive real
part (collapse of model) or there is some eigenvalue along the imaginary axes so near to zero
(real part) that it can approach through some perturbation the imaginary axis. We look for
resolution of approximation (3) as Taylor series coefficients.

\[ \rho = \sum_{n} \lambda^{n} \rho^{(n)} \]

The important difference as compared to Taylor series of solution (13) is that we explicitly
assume existence of perturbation of the order \( \lambda^{3} \), respectively \( \eta \lambda^{2} \), which is otherwise arbi-
trary. We take only the results which are independent of potential perturbation. However,
this is a standard correct perturbational method. Such a treatment gives us only finite
number of conditions for Taylor coefficients. The calculation is straightforward. Condition
in the zeroth order enables the calculation of

\[ \rho_{12}^{(0)} = 0; \quad \rho_{14}^{(0)} = 0; \quad \rho_{23}^{(0)} = 0; \quad \rho_{34}^{(0)} = 0, \]

while in the second order

\[ \rho_{13}^{(0)} = 0; \quad \rho_{24}^{(0)} = 0; \quad \rho_{12}^{(2)} = 0; \quad \rho_{14}^{(2)} = 0; \quad Im \rho_{23}^{(2)} = 0; \quad Re \rho_{23}^{(2)} = J(\rho_{33}^{(0)} - \rho_{22}^{(0)}), \]

\[ \rho_{11}^{(0)} = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} \rho_{22}^{(0)}; \quad \rho_{44}^{(0)} = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} \rho_{33}^{(0)}. \]  

(21)

Here we clearly see the internal problem of the second order approximation (3). Neither
the zeroth order of the density matrix is resolved by stationary condition (10). We have
still a two-dimensional subspace (arbitrary \( \rho_{22}^{(0)}; \rho_{33}^{(0)} \)) where the steady state can be found
(in the Liouville space of the density matrix). The result (13) is the corollary of implicit
assumption of zero effect of higher order calculation, not justifiable from the mathematical
point of view. One can comprehend that including a potentially higher order perturbation
like (16) will define the zeroth order density matrix in space of our result (21) with a high
degree of arbitrariness.

The solution, which is correct to at least the zeroth order and would have to be stable
against perturbations, one must calculate more precisely.

We notice that including the perturbation not as a potentiality, but like a real effect
changes the stability of the model. One can prove in both interpretations that we obtain
further condition (once, in the order \( \lambda^4 \) or respectively \( \eta \lambda^2 \))

\[ g_1 \rho^{(0)}_{22} = g_4 \rho^{(0)}_{33}. \]

In the first interpretation we obtain in the fourth order also further conditions; however, because of its speculative character we will not publish it here. This means that the situation, despite of its unpleasant character, is not hopeless. One can indicate instability and also the ways to improve models are principally possible. Let us notice that the result obtained in this subsection is in accordance with all previous calculations in \( \lambda \to 0 \) limit.

V. THE VAN HOVE LIMIT

All our previous results were obtained in a way that is not just standard in relaxation theory. We introduced perturbational scheme (9) for calculation of the second order kinetic equation for model Hamiltonian (1). We gave some physical arguments for this choice. Nevertheless, the standard variant of great popularity is of course the van Hove limit [12]:

\[ J \propto 1, \Gamma_\uparrow, \Gamma_\downarrow \propto \lambda^2. \]  

(22)

We argue here that the problem with infinite time asymptotics of the model (1) (in the second order kinetic equation) is reflected also in this well understood limit. To see this we introduce ” energetic” representation in eigenvectors of \( H_S \)

\[ c_{\Pi} = \alpha c_2 - \beta c_3, \quad c_{\Pi III} = \alpha c_3 + \beta c_2 \]

(23)

where:

\[ \alpha = \frac{\sqrt{2}(1 + \sqrt{1 + 4J^2 / \epsilon^2})}{2 \sqrt{4J^2 / \epsilon^2} + 1 + \sqrt{4J^2 / \epsilon^2} + 1} \propto 1, \quad \beta = \frac{\sqrt{2}J}{\epsilon \sqrt{4J^2 / \epsilon^2} + 1 + \sqrt{4J^2 / \epsilon^2} + 1} \propto \frac{J}{\epsilon} \]

The model (1) is now:

\[ H = \epsilon c_{\Pi}^\dagger c_1 + \frac{\epsilon}{2}(1 + \sqrt{1 + \frac{4J^2}{\epsilon^2}})c_{\Pi III} c_{\Pi III} + \frac{\epsilon}{2}(1 - \sqrt{1 + \frac{4J^2}{\epsilon^2}})c_{\Pi}^\dagger c_1 + \sum_k \{ \Omega_k B_k^\dagger B_k + G_k^{(1-2)}(B_k c_{\Pi}^\dagger (\alpha c_{\Pi III} + \beta c_{\Pi III}) + B_k^\dagger (\alpha c_{\Pi III}^\dagger + \beta c_{\Pi III}^\dagger) c_1) + G_k^{(3-4)}(B_k (\alpha c_{\Pi III}^\dagger - \beta c_{\Pi III}^\dagger)c_4 + B_k^\dagger c_4^\dagger (\alpha c_{\Pi III} - \beta c_{\Pi III})) \} \]

(24)

We offer some comments regarding Hamiltonian (24) and the van Hove limit (22). There are two bath induced channels between levels 1,II and III,4 respectively, in analogy with the
previous treatment in site representation. What is the difference is that there is no coherent transfer term in energetic representation; on the other hand two weak bath induced channels between levels 1,III and II,4 appeared. The strength of these channels is proportional to $(JG)^2$, so this term is in the second order kinetic theory of relevance in the van Hove limit only. (The region of physical applicability of (22) does not contain the regime specified before in connection with (9). We only clarify behavior of treated model hamiltonian from another view.) These channels cause communication between specified levels for short time regime, nevertheless both the channels lie off the energy shell, so for the long time regime this transfer is forbidden. Then the second order kinetic theory with integrated memory like (22) in infinite time forbids all the communication between pair of levels 1+II and that of levels III+4. Asymptotical stationary condition then has two linearly independent solutions. Nevertheless

$$c_1^\dagger c_1 + c_{II}^\dagger c_{II}$$

does not commute with the full Hamiltonian (24), it is no integral of motion. Consequently one can not use the long time (Born-Markov) approximation upon looking for time asymptotics - the result may depend also on short time transient effects. The result obtained in this way is also seemingly unstable against higher order calculation. In Appendix B we give the complete second order kinetic equation and its solution in the van Hove scheme. The solution (B9) of stationary condition (10) shows just the same asymptotic state of the density matrix (and potential instability) like (21).

We stay here at quite real physical problem: Consideration whether these levels are isolated and the transfer is strictly forbidden, what suggests ordinary meaning of the energy conservation law, or whether a limited value of electron density can be transferred. The significance of the van Hove limit is here also questioned.

Last but not least, we may also think about more symmetrical case of system - bath coupling of form:

$$\sum_k \{G_k^{(1-2)}(B_k + B_k^\dagger)(c_1^\dagger c_2 + c_2^\dagger c_1) + G_k^{(3-4)}(B_k + B_k^\dagger)(c_3^\dagger c_4 + c_4^\dagger c_3)\}.$$  

The result for (9) remains unchanged. Then in energy representation also 1,III and II,4 channels appear that lie on energy shell for interaction with low energy phonons, if these are present. Then the asymptotics in the van Hove limit can be obtained as unique. However, the existence of such phonons (and channels) is a serious change in physical meaning of the
entering model. Inapplicability of the van Hove approach for physical regime $J < G^2$ is apparent.

VI. PHYSICAL CONSEQUENCES AND CONCLUSIONS

Let us firstly discuss some physical consequences of possible instability in the first scheme (18). We have shown that the result obtained in the second order may be unstable against some correction arising in a higher order calculation. Let us stay on the position that evolution generator (Hamiltonian) is exact, and the only question is the correctness of its study. Of course, in that case, our construction of higher order correction is rather speculative, but it proved the instability of the result. The full analysis of the spectrum of the transfer matrix showed that the most ‘slow excitation of the steady state’ calculated in the second order has its lifetime of the sixth order in $\lambda$. This gives that also in the case where first correction to terms $W_{\{22\}}^{\{33\}}, W_{\{33\}}^{\{22\}}$ is of the order six, it may cause such an instability. This questions some standard results obtained in everyday simulations. Unfortunately we have also some intuitive physical arguments that one must really calculate at least six order processes for achievement reliable result for transfer between 2-3 sites. This is because the transfer rate really is a process (at least) of the 6th order in specified scheme (18). Incoherent transfer term between sites 2 and 3 lies off energy-shell, consequently some collaboration with bath modes for stabilization is necessary. All the Feynman graphs one can draw must have for such a transfer great number of lines in order to get on energetic sphere, implying high order of this transfer. The reported delicate situation in the van Hove limit also supported caution against straightforward use of kinetic theory. Unfortunately, any higher order contribution calculation is a difficult task, getting dramatically worse from order to order. This fact will also in future cause the great popularity of the ”naive” treatment; in this direction, our expectation concerning influence of our work is rather pessimistic. Greater care about applicability of usual model methods is, on the other hand and in the light of our results, more than appropriate. Further investigation should be turned to higher order inspection of master equation connected with Hamiltonian in specified physical regime. Especially the question connected with the infinite time asymptotics is a great challenge, of crucial physical implication, and not satisfactorily resolved yet.
Acknowledgments

The present author is indebted to Prof. V. Čápek for his careful reading of the manuscript and valuable discussions concerning subject of this paper. Support of grants 202/99/0182 of the Czech grant agency and 153/1999/B of the Grant agency of Charles University is gratefully acknowledged.

APPENDIX A: DETAILED ANALYSIS OF SPECTRUM

Determination of the twelve eigenvalues does not meet with problems, because these are the roots of quadratic polynomials. In addition we would like mainly to know signs of real parts of the eigenvalues, at least in the limit $\lambda \to 0$. Thus we reduce complicated results into the Taylor series at least to the order which gives the sign:

$$\xi_1 = 0, \quad \xi_2 = -\Gamma_\uparrow - \Gamma_\downarrow$$

$$\xi_7 = -i\frac{\epsilon}{2} - \frac{3\Gamma_\downarrow + \Gamma_\uparrow}{4} + i\sqrt{\frac{\epsilon^2}{4} + i\epsilon \frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4}} + J^2 \approx -\Gamma_\downarrow$$

$$\xi_8 = -i\frac{\epsilon}{2} - \frac{3\Gamma_\downarrow + \Gamma_\uparrow}{4} - i\sqrt{\frac{\epsilon^2}{4} + i\epsilon \frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4}} + J^2 \approx -i\epsilon - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2}$$

$$\xi_{11} = -i\frac{\epsilon}{2} - \frac{3\Gamma_\uparrow + \Gamma_\downarrow}{4} + i\sqrt{\frac{\epsilon^2}{4} - i\epsilon \frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4}} + J^2 \approx -i\epsilon - \frac{\Gamma_\uparrow + \Gamma_\downarrow}{2}$$

$$\xi_{12} = -i\frac{\epsilon}{2} - \frac{3\Gamma_\uparrow + \Gamma_\downarrow}{4} - i\sqrt{\frac{\epsilon^2}{4} - i\epsilon \frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4}} + J^2 \approx -\Gamma_\uparrow$$

$$\xi_{15} = i\epsilon - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2}$$

$$\xi_9 = \xi_7^*; \quad \xi_{10} = \xi_8^*; \quad \xi_{13} = \xi_{11}^*; \quad \xi_{14} = \xi_{12}^*; \quad \xi_{16} = \xi_{15}^*$$

Further eigenvalues are roots of the 4-th order polynomial coming from the submatrix A. Though there is a formula which enables explicitly to extract the roots - so called Cardano formula, we do not use it because of its complicated form, and we only determine leading terms of the limit case $\lambda \to 0$ using the Taylor series. (This point provides no additional assumption about analytical structure of this dependence, all the results can be proved using mean value theorem.)

$$\xi_3 \approx -\Gamma_\uparrow - \Gamma_\downarrow; \quad \xi_4 \approx -\frac{J^2(\Gamma_\uparrow + \Gamma_\downarrow)}{\epsilon^2}$$
\[ \xi_5 \approx i\epsilon - \frac{\Gamma_\uparrow + \Gamma_\downarrow}{2}; \quad \xi_6 = \xi_5^* \]

Notice: The complex square root used in formulae above is defined into the upper half-plane of the complex plane (e.g. \(\text{Im}\sqrt{ } \geq 0\)).

**APPENDIX B: TIME ASYMPTOTICAL SOLUTION OF THE SECOND ORDER KINETIC EQUATION OF MODEL IN VAN HOVE LIMIT**

We start from (24) and in the van Hove perturbational scheme (22). Organization of column vector of the density matrix is following:

\[ \rho^T = (\rho_{11}, \rho_{II,II}, \rho_{III,III}, \rho_{44}, \text{Re}\rho_{II,III}, \text{Im}\rho_{II,III}, \text{Re}\rho_{1,II}, \text{Im}\rho_{1,II}, \text{Re}\rho_{1,III}, \text{Im}\rho_{1,III}) \]

Kinetic equations (2) obtained here from e.g. (6) are:

\[
W^{(2)} = \begin{pmatrix}
A & 0 & 0 & 0 \\
0 & B & 0 & 0 \\
0 & C & 0 & 0 \\
0 & 0 & 0 & D
\end{pmatrix}
\]

where

\[
A = \begin{pmatrix}
-\Gamma_\downarrow^u & \Gamma_\uparrow^u & 0 & 0 & \theta \Gamma_\uparrow^u & 0 \\
\Gamma_\downarrow^u & -\Gamma_\uparrow^u & 0 & 0 & \theta \Gamma_\downarrow^u & 0 \\
0 & 0 & -\Gamma_\downarrow^u & \Gamma_\uparrow^u & -\theta \Gamma_\downarrow^u & 0 \\
0 & 0 & \Gamma_\downarrow^u & -\Gamma_\uparrow^u & -\theta \Gamma_\downarrow^u & 0 \\
\frac{\sigma \Gamma_\uparrow^u}{2} - \frac{\sigma \Gamma_\downarrow^u}{2} & \frac{\sigma \Gamma_\uparrow^u}{2} & -\frac{\sigma \Gamma_\uparrow^u}{2} & -\frac{\Gamma_\uparrow^u + \Gamma_\downarrow^u}{2} -\epsilon - 2\Delta \\
0 & 0 & 0 & 0 & \epsilon + 2\Delta & -\frac{\Gamma_\uparrow^u + \Gamma_\downarrow^u}{2}
\end{pmatrix}
\]

\[
B = \begin{pmatrix}
-\frac{\Gamma_\uparrow^u + \Gamma_\downarrow^u}{2} & \epsilon + \Delta & \frac{\sigma \Gamma_\uparrow^u}{2} & 0 \\
-\epsilon - \Delta & -\frac{\Gamma_\uparrow^u + \Gamma_\downarrow^u}{2} & 0 & \frac{\sigma \Gamma_\uparrow^u}{2} \\
-\frac{\sigma \Gamma_\uparrow^u}{2} & 0 & -\Gamma_\downarrow^u & -\Delta \\
0 & -\frac{\sigma \Gamma_\uparrow^u}{2} & \Delta & -\Gamma_\downarrow^u
\end{pmatrix}
\]
\[ C = \begin{pmatrix} -\frac{\Gamma_{v}^u + \Gamma_{v}^d}{2} & \epsilon + \Delta & -\frac{\theta \Gamma_{v}^u}{2} & 0 \\ -\epsilon - \Delta & -\frac{\Gamma_{v}^u + \Gamma_{v}^d}{2} & 0 & -\frac{\theta \Gamma_{v}^u}{2} \\ \frac{\theta \Gamma_{v}^u}{2} & 0 & -\Gamma_{v}^d & -\Delta \\ 0 & -\frac{\theta \Gamma_{v}^u}{2} & +\Delta & -\Gamma_{v}^d \end{pmatrix}, \quad D = \begin{pmatrix} -\frac{\Gamma_{v}^u + \Gamma_{v}^d}{2} & \epsilon \\ -\epsilon & -\frac{\Gamma_{v}^u + \Gamma_{v}^d}{2} \end{pmatrix}. \] (B4)

where:

\[ \Delta = \frac{\epsilon}{2} \left( \sqrt{\frac{4J^2}{\epsilon^2} - 1} \right) \]
\[ \theta = \frac{\beta}{\alpha} = \frac{2J}{\epsilon(1 + \sqrt{1 + \frac{4J^2}{\epsilon^2}})} \]
\[ \Gamma_{v}^u = 2\pi \alpha^2 \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon + \Delta - \Omega_k) \text{Tr}_{\text{Bath}} \rho_{\text{Bath}}(B^\dagger_k B_k) \]
\[ = 2\pi \alpha^2 \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon + \Delta - \Omega_k) \text{Tr}_{\text{Bath}} (\rho_{\text{Bath}} B^\dagger_k B_k) \]
\[ \Gamma_{v}^d = 2\pi \alpha^2 \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon + \Delta - \Omega_k) \text{Tr}_{\text{Bath}} (\rho_{\text{Bath}} B_k B^\dagger_k) \]
\[ = 2\pi \alpha^2 \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon + \Delta - \Omega_k) \text{Tr}_{\text{Bath}} (\rho_{\text{Bath}} B_k B^\dagger_k). \] (B5)

One can verify that stationary condition (10) is satisfied by density matrix:

\[ \rho = C \left( \frac{\Gamma_{v}^u}{\Gamma_{v}^u + \Gamma_{v}^d} c_1^\dagger c_1 + \frac{\Gamma_{v}^d}{\Gamma_{v}^u + \Gamma_{v}^d} c_\Pi^\dagger c_\Pi \right) + (1 - C) \left( \frac{\Gamma_{v}^u}{\Gamma_{v}^u + \Gamma_{v}^d} c_\Pi^\dagger c_\Pi + \frac{\Gamma_{v}^d}{\Gamma_{v}^u + \Gamma_{v}^d} c_4^\dagger c_4 \right) \] (B6)

with arbitrarily chosen constant \( C \in (0, 1) \).

This proves the statement of main text.
[1] F. Šanda to be published elsewhere.

[2] R. Balescu, Equilibrium and Nonequilibrium Statistical Mechanics (J.Wiley and Sons Inc., New York-London-Sydney-Toronto, 1975).

[3] W. Brenig, Statistical Theory of Heat: Nonequilibrium Phenomena (Springer-Verlag,Berlin-Heidelberg 1989).

[4] S. Fujita, Introduction to Nonequilibrium Quantum Statistical Mechanics(W.B. Saunders Company,Philadelphia-London 1966).

[5] R. Zwanzig, Physica 30 (1964) 1109.

[6] M. Tokuyama and H. Mori, Progr. Theor. Phys. 55 (1976) 411.

[7] H. Bauer, Probability Theory, (Walter de Gruyter, Berlin-New York, 1996).

[8] V. Čapek, Czech. J. Phys. 42 (1992) 317.

[9] R. Balescu, Physica 27 (1961) 693.

[10] R. Swenson, Physica 29 (1963) 1147.

[11] E. B. Davies, Quantum Theory of Open Systems (Academic Press, London, 1976).

[12] L. van Hove, Physica 21 (1955) 517.; ibid. 23 (1957) 441.

[13] V. Čapek, I. Barvík, Physica A 294 (2001) 388.

[14] H. Haken, G. Strobl, "Exact Treatment of Coherent and Incoherent Triplet Exciton Migration" in The Triplet State, ed. by A.Zahlan (Cambridge Univ. Press, London, 1967) p. 311-314.

[15] P. Reineker, H. Haken "The Coupled Coherent and Incoherent Motion of Frenkel Exciton in Molecular Crystals" in Localization and Delocalization in Quantum Chemistry, Vol. II ed. by O.Chalvet, R. Daudel, R. Diner, P. Malrieu (Reidel, Dortrecht, Boston 1976) pp. 185.-194.

[16] V. Čapek, http://arxiv.org/abs/cond-mat/0012056, Europ. Phys. Journal B (2002) - in press.