

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

F Šanda

Institute of Physics of Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5,
121 16 Prague 2, Czech Republic

E-mail: sanda@karlov.mff.cuni.cz

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Abstract

The kinetic model of an open system, which embodies an instability in long time regime behaviour, is referred. This result questions some approximations which are standardly used in open system treatments. The deficiency in kinetic treatments was recently referred to as mainly a mathematical curiosity [1]; however, in the present work the application for a physically comprehensive situation is shown. We simplified the previously treated model, which enables us to proceed easily with just pen and paper and to omit numerical modelling whose justification causes difficulties to the reader. We draw some consequences on the found instability, both with respect to the perturbative origin of kinetic equations and also concerning the very philosophy of physical modelling.

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1. Introduction

The subject of the present paper is new results questioning the stability of solutions to kinetic equations. Kinetic equations are widely used in solid state or statistical physics in modelling transfer processes including relaxation phenomena, the influence of external fields, etc. This concerns a great number of physical theories appropriate for different physical regimes of interest such as the Boltzmann equation [2], the Fokker–Planck equation [3, 4], the Pauli master equation [5] or its generalized versions introduced independently in different forms by Zwanzig and Mori [6, 7], etc. The general mathematical structure of these theories is the set of differential or integro-differential equations (of first order), which determines the time evolution of quantities of interest. In the easiest case we meet a time independent Markov process (without memory), however, otherwise the equations may contain time dependences in coefficients (for example, dependence on external fields), memory terms (time nonlocal equations) or inhomogeneous terms or nonlinearity.

Instabilities or chaotic behaviour in the case of complicated nonlinear equations is surely not very surprising. Below, we deal with the easiest form of kinetic equations—the set of linear differential equations with constant coefficients. The specific topic of the present work is scrutiny of steady state stability, including that of the attractor nature of the steady state. Let us make some comments here on how this treatment is related to other types of mathematical structures which are also used in physically similar treatments, and about physical consequences of this work. Time-local and memory-including theories of Markov processes are related in general (for the general mathematical theory, see for example [8]) and also explicit equivalence for specific types of equations stemming from the Liouville equation could be found [9, 10]. The goal of the cited works 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 an evolution matrix) often turn into time independent ones in the infinite time region [11, 12]. Some kind of Markov approximation here becomes exact. This provides the connection with our work. The influence of external fields is a further property that can often be related to our topic of interest.

The kinetic equations have their origin in formal identities, which turn fundamental microscopical physical laws into differential equations determining the time evolution of macroscopic quantities available in experiments. For practical reasons, the exact formal identity needs to be approximated by calculation of leading terms of the Taylor series in some chosen perturbational parameter for rate coefficients of master equations, or similarly by a cut in the BBGKY hierarchy in the case of the Boltzmann equation. Consequently, the kinetics models are an approximation to an impossible full treatment. It is quite usual to use the approximation of the second order in coupling to uncontrolled degrees of freedom, which enables us to incorporate connected relaxation phenomena.

The time evolution of ‘quantities of physical interest’ is then solved, following the particular kinetic equation. Formally, the validity of all these approximations of perturbational origin is limited to the time axis. On the other hand, these are the steady state and the asymptotic limits which are of greatest physical importance. Otherwise well applicable theory is thus asked to provide reasonable results also for this time region. Expected results such as the Boltzmann distribution were found in the simplest kinetic models, which gave physicists a strong belief in the general applicability of the particular kinetic theory. The limitation of the perturbative treatment is underestimated by the statement that small changes of coefficients cannot change results of numerical studies in very dramatic way, which is usually considered as ‘physically reasonable’. However, this ‘statement’ is *not* true. We want to show that such a difficulty is more frequent in numerical kinetic modelling than is usually considered. This is by no means only of mathematical interest, a related situation was noted, e.g., in [13]; also, this paper has its birth from the sequence of papers cited below.

Recently we pointed out (in [1]) that some mathematics connected with kinetic models does not guarantee the appropriate description in the long time region. In particular, the solution to the second order kinetic equation, which is proved to approximate the right density matrix in the sense of Davies theorems [14, 15], is instable to potential higher order contributions to rate coefficients. The arguments were developed on the background of the treatment of a relatively simple model consisting of two sites with vibrational levels. This calls for further simplification of the model and physical comprehension of the stated arguments. It is just the goal of this work and we would like to warn the reader against unexpected features encountered in this problem. When one incorporates (according to his/her opinion) all the important physical processes into a kinetic model, attention must be also focused on the stability of the solution. In particular, the question is which part of the results is guaranteed and what is only a belief (and contingently only an unjustified belief). In the case when

the resulting steady state cannot be confronted with well established, e.g., thermodynamical laws, the result of thus questionable simulation may seem to be quite good. Sometimes belief in the second order approximation results lies in sophisticated mathematical methods which pretend to give a ‘general’ proof of correctness of the second order results without any realistic treatment of the stability, case by case. Such methods might, regardless of their mathematical validity and usefulness, leave wide scope for speculations about their credibility in concrete applications, in some important features of the solution, such as in our model from [1].

The treated model stems from open kinetic models in the strong coupling regime, which was investigated in [16, 17] (and citations therein). The regime was formally described by modified Davies theory [18]. The authors of [17] have found some surprising features of the asymptotical solution where it is argued that beyond the weak coupling limit, their system (according to calculation) does not follow the canonical distribution in the long time domain. We show that their conclusion had no rigorous mathematical ground, and some of their statements need to be proved with additional mathematical care. Moreover, the very easy form of the present model enlightens the physical origin of such a result.

We outline in the present work a calculation similar to [16, 17] and show that attachment of an additional process, which is formally infinitely slower, changes the asymptotic in a dramatic way. This idea is presented on a simple model. All the calculations are done manually and the reader is 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. This is in particular important when a complicated model is investigated whose analytical treatment is impossible, but where only computer simulations are at hand.

2. Model

A four site open system is described by a Hamiltonian

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

We measure energy in units of \hbar . The Hamiltonian describes a 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 and the remaining one being coherent. The system (1) is related to the recently reported one, if the vibrational structure over each site, introduced in [1], is limited to the ground level and the first excited level. As long as we consider one particle only, there is no necessity to introduce (anti)commutational relations between these operators. The dynamics of the system is dominated by bath induced transfer channels between 1–2 and 3–4 sites and the coherent transfer channel 2–3. B_k^\dagger, B_k are creation and annihilation operators of the k th bath phonon mode (fulfilling the boson commutational relation), and $G_k^{(i-j)}$ are coupling constants of the system–bath interaction. Parameter J describes the strength of the coherent channel.

We do not allow any interference between the bath-induced channels 1–2 and 3–4, which means fulfilling conditions such as

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

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 magnitudes of the coefficients in the Hamiltonian. Here we are interested in the regime where it is appropriate to treat the J - and bath-induced transfer channels as a perturbation. We emphasize that this choice does not correspond to the so-called van Hove limit [19, 20]. One can diversify the physical interpretation of Hamiltonian (1) and a chosen perturbation scheme. One can consider the coherent channel as a slow internal motion treated according to [18], but it may also represent constant or periodical external field influence.

Various constructions of kinetic equations can also be applied. We restrict ourselves to those which respect the chosen mathematical structure and the physical regime. Though here also physicists use various formalisms, one may obtain our results using the Nakajima–Zwanzig identity (in the Born–Markov approximation) [6], the Tokuyama–Mori equation (in its standard second order formulation) [7] and also the Haken–Strobl–Reineker parametrization [21, 22], all of which lead here to formally the same master equation:

$$\frac{d\rho_{ij}}{dt} = \sum_{\{kl\}} W_{\{ij\},\{kl\}} \rho_{\{kl\}} \quad (2)$$

where vector ρ is organized in the following way

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

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

$$W^{(2)} = \begin{pmatrix} A & 0 & 0 & 0 \\ 0 & B & 0 & 0 \\ 0 & 0 & C & 0 \\ 0 & 0 & 0 & D \end{pmatrix} \quad (3)$$

where

$$A = \begin{pmatrix} -\Gamma_{\downarrow} & \Gamma_{\uparrow} & 0 & 0 & 0 & 0 \\ \Gamma_{\downarrow} & -\Gamma_{\uparrow} & 0 & 0 & 0 & -2J \\ 0 & 0 & -\Gamma_{\downarrow} & \Gamma_{\uparrow} & 0 & 2J \\ 0 & 0 & \Gamma_{\downarrow} & -\Gamma_{\uparrow} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & -\epsilon \\ 0 & J & -J & 0 & \epsilon & -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} \end{pmatrix} \quad (4)$$

$$B = \begin{pmatrix} -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & \epsilon & 0 & -J \\ -\epsilon & -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & J & 0 \\ 0 & -J & -\Gamma_{\downarrow} & 0 \\ J & 0 & 0 & -\Gamma_{\downarrow} \end{pmatrix} \quad (5)$$

$$C = \begin{pmatrix} -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & \epsilon & 0 & J \\ -\epsilon & -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & -J & 0 \\ 0 & J & -\Gamma_{\uparrow} & 0 \\ -J & 0 & 0 & -\Gamma_{\uparrow} \end{pmatrix} \quad (6)$$

$$D = \begin{pmatrix} -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} & \epsilon \\ -\epsilon & -\frac{\Gamma_{\uparrow}+\Gamma_{\downarrow}}{2} \end{pmatrix}. \quad (7)$$

Here

$$\begin{aligned}
 \Gamma_{\uparrow} &= 2\pi \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{bath}}(\rho_{\text{bath}} B_k^{\dagger} B_k) \\
 &= 2\pi \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{bath}}(\rho_{\text{bath}} B_k^{\dagger} B_k) \\
 \Gamma_{\downarrow} &= 2\pi \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{bath}}(\rho_{\text{bath}} B_k B_k^{\dagger}) \\
 &= 2\pi \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon - \Omega_k) Tr_{\text{bath}}(\rho_{\text{bath}} B_k B_k^{\dagger}).
 \end{aligned}
 \tag{8}$$

The equality of the coefficients for 1–2 and 3–4 transfer is our additional assumption, which cannot be deduced from (1). (The potential discussion concerning imaginary memories is excluded by the demand that the density of phonons is symmetrical around ϵ . However, neither can such terms change any conclusion given below.) Note that $J, \Gamma_{\uparrow}, \Gamma_{\downarrow}$ are considered as perturbations of the same magnitude, proportional to the parameter λ^2

$$J, \Gamma_{\uparrow}, \Gamma_{\downarrow} \propto \lambda^2.
 \tag{9}$$

(The reason for this proportionality is only consistency with the standard perturbational order of the bath-induced transfer channels.)

The steady state is given by the condition

$$\sum_{\{kl\}} W_{\{ij\},\{kl\}} \rho_{\{kl\}} = 0.
 \tag{10}$$

We now calculate the complete spectrum of the evolution matrix. Firstly, this enables us to show that the 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 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 quasideagonal structure. We have to calculate a characteristic equation. After a bit of algebra (we must calculate determinants of submatrices of maximal order 6) and rearranging resulting terms, we obtain¹

$$\begin{aligned}
 0 &= \xi \cdot (\xi + \Gamma_{\uparrow} + \Gamma_{\downarrow}) \cdot \left\{ \xi(\xi + \Gamma_{\uparrow} + \Gamma_{\downarrow}) \left[\left(\xi + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right)^2 + \epsilon^2 \right] + 4J^2 \left(\xi + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right)^2 \right\} \\
 &\times \left\{ \left(\xi + i\epsilon + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right) (\xi + \Gamma_{\downarrow}) + J^2 \right\} \cdot \left\{ \left(\xi - i\epsilon + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right) (\xi + \Gamma_{\downarrow}) + J^2 \right\} \\
 &\times \left\{ \left(\xi + i\epsilon + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right) (\xi + \Gamma_{\uparrow}) + J^2 \right\} \cdot \left\{ \left(\xi - i\epsilon + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right) (\xi + \Gamma_{\uparrow}) + J^2 \right\} \\
 &\times \left[\left(\xi + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \right)^2 + \epsilon^2 \right].
 \end{aligned}
 \tag{11}$$

Twelve roots can be calculated directly from the quadratic terms. What remains is a polynomial equation of fourth order. The roots can in principle also be extracted using the Cardano formula, but it does not provide an easy survey. Instead, we inspect the behaviour in the $\lambda \rightarrow 0$ limit

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

of the perturbational parameter. This analysis and the calculation of 12 exact eigenvectors are provided in appendix A.

In conclusion, there is only one steady state and, at least not for small values of parameter λ , all the other eigenvalues of matrix (3) have negative real parts, i.e. connected terms in time evolution simulation disappear in infinite time and the steady state is also the asymptotical one. Because of the finite dimension of the matrix, there is a region surrounding $\lambda = 0$ where evolution has infinite time asymptotics given by (10), so one can limit oneself to this region without complications. For very high values of the parameter λ , the model need not have the correct behaviour in accordance with the general inapplicability of the perturbational treatment for this case. It is worth noting that the zero eigenvalue was obtained purely from the first submatrix 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.

The solution to steady state condition (10) is calculated concerning the normalization condition

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

It yields

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

We specifically note the equality in population at sites 2 and 3.

The relaxation does not steer for the canonical asymptotics here as the system need not be in thermodynamic equilibrium. The 2–3 channel is elastic which implies 2–3 symmetry and consequent equality $\rho_{22} = \rho_{33}$. This is a consequence of omitting the van Hove limit. The potentially external character of the term J can be comprehended as responsible. Attention can also be focused on dissolution of the van Hove limit and strong coupling regime in [16, 17]. In fact, we obtained an exactly similar result as in [17]. There is no evident internal collapse in these calculations.

3. Perturbation

In this section a small perturbation of model (1) is introduced in the form of an incoherent transfer channel between sites 2 and 3. The new terms in evolution matrix may be quite small with respect to the others obtained from the previous consideration. Construction of the terms is fully analogous to the previous case. Formally, a change can be included in the 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 present a new corrected evolution matrix; the effectiveness of the new 2–3 channel is measured by rate coefficients $g_{\uparrow}, g_{\downarrow}$:

$$A = \begin{pmatrix} -\Gamma_{\downarrow} & \Gamma_{\uparrow} & 0 & 0 & 0 & 0 \\ \Gamma_{\downarrow} & -\Gamma_{\uparrow} - g_{\uparrow} & g_{\downarrow} & 0 & 0 & -2J \\ 0 & g_{\uparrow} & -\Gamma_{\downarrow} - g_{\downarrow} & \Gamma_{\uparrow} & 0 & 2J \\ 0 & 0 & \Gamma_{\downarrow} & -\Gamma_{\uparrow} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} & -\epsilon \\ 0 & J & -J & 0 & \epsilon & -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \end{pmatrix} \quad (14)$$

$$B = \begin{pmatrix} -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow}}{2} & \epsilon & 0 & -J \\ -\epsilon & -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow}}{2} & J & 0 \\ 0 & -J & -\Gamma_{\downarrow} - \frac{g_{\downarrow}}{2} & 0 \\ J & 0 & 0 & -\Gamma_{\downarrow} - \frac{g_{\downarrow}}{2} \end{pmatrix} \quad (15)$$

$$C = \begin{pmatrix} -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\downarrow}}{2} & \epsilon & 0 & J \\ -\epsilon & -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\downarrow}}{2} & -J & 0 \\ 0 & J & -\Gamma_{\uparrow} - \frac{g_{\uparrow}}{2} & 0 \\ -J & 0 & 0 & -\Gamma_{\uparrow} - \frac{g_{\uparrow}}{2} \end{pmatrix} \quad (16)$$

$$D = \begin{pmatrix} -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} & \epsilon \\ -\epsilon & -\frac{\Gamma_{\uparrow} + \Gamma_{\downarrow}}{2} \end{pmatrix}.$$

Now we calculate the stationary state of problem (16). The assumption that λ is so small that submatrices B , C and D are regular holds and so the stationary condition applied here has the trivial solution only. Then, one gets the result after easy algebra:

$$\begin{aligned} \rho_{11} &= C \Gamma_{\uparrow}^2 \left\{ g_{\downarrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2 \right\} \\ \rho_{22} &= C \Gamma_{\downarrow} \Gamma_{\uparrow} \left\{ g_{\downarrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2 \right\} \\ \rho_{33} &= C \Gamma_{\downarrow} \Gamma_{\uparrow} \left\{ g_{\uparrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2 \right\} \\ \rho_{44} &= C \Gamma_{\downarrow}^2 \left\{ g_{\uparrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2 \right\} \\ \text{Re } \rho_{23} &= C \frac{-2\epsilon J (g_{\downarrow} - g_{\uparrow}) \Gamma_{\downarrow} \Gamma_{\uparrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow})} \\ \text{Im } \rho_{23} &= C J (g_{\downarrow} - g_{\uparrow}) \Gamma_{\downarrow} \Gamma_{\uparrow} \end{aligned}$$

where C is a normalization constant to be deduced from (12):

$$\begin{aligned} \frac{1}{C} &= 2 * J^2 (\Gamma_{\uparrow} + \Gamma_{\downarrow})^2 + \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) \\ &\quad \times (\Gamma_{\uparrow} + \Gamma_{\downarrow}) (\Gamma_{\uparrow} g_{\downarrow} + \Gamma_{\downarrow} g_{\uparrow}). \end{aligned}$$

We are interested especially in the ratio of the populations on sites 2 and 3. The reason for this specific interest becomes apparent later:

$$\frac{\rho_{22}}{\rho_{33}} = \frac{g_{\downarrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2}{g_{\uparrow} \left(\frac{2\epsilon^2}{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}} + \frac{\Gamma_{\uparrow} + \Gamma_{\downarrow} + g_{\uparrow} + g_{\downarrow}}{2} \right) + 2J^2}. \quad (17)$$

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; the first of these is submitted mainly for a mathematically oriented reader. We consider g_{\uparrow} , g_{\downarrow} as proportional to λ^4 :

$$J, \Gamma_{\downarrow}, \Gamma_{\uparrow} \propto \lambda^2 \quad g_{\uparrow}, g_{\downarrow} \propto \lambda^4. \quad (18)$$

One may have some objections against this interpretation, stemming from the fact that we did not provide complete fourth order inspection of the kinetic theory. But here our objective is

limited. We point out the instability of the result (13) against the fourth order correction, which is considered to be arbitrary—as a potentiality. We argue that an arbitrary perturbation could be used to achieve this conclusion. The 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 δH , and think of the perturbation as consisting of higher order terms obtained potentially from the Hamiltonian (1) that are omitted in standard second order calculation. The results (13) and (16) will be compared in the $\lambda \rightarrow 0$ limit where the perturbational treatment is best verified. (Performing this limit has, of course, no consequence in connection with the main statement—instability).

In the second interpretation we consider the perturbation to be formally of the second order, but of small magnitude. We introduce an additional parameter η that measures the relative power of different transfer channels

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

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

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

where ρ designates here the steady state in the $\lambda \rightarrow 0$ limit. This is the central statement that we are going to prove. The stability of standard kinetic equations is inspected with respect to physical processes which were not incorporated into a model in question because of their low strength (at least from a formal, cursory point of view) and consequent underestimation of their influence. This point is possibly not so interesting mathematically because the second order theory holds here, but it seriously questions the straightforward applicability of the standard kinetics from a physical point of view. Both these interpretations are quite distinct mathematically and physically. We argue that the unstable behaviour is the internal problem of the approximation (3) and does not come from the very specialized choice of perturbation or scheme of treatment. In the next section we make this point clearer.

Performing the announced limits. First interpretation (18):

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

Second interpretation (19):

$$\begin{aligned} \lim_{\eta \rightarrow 0} \lim_{\lambda \rightarrow 0} \frac{\rho_{22}}{\rho_{33}} &= \lim_{\eta \rightarrow 0} \lim_{\lambda \rightarrow 0} \frac{\eta \lambda^2 g_{\downarrow} \left(\frac{2\epsilon^2}{\lambda^2[\Gamma_{\uparrow} + \Gamma_{\downarrow} + \eta(g_{\uparrow} + g_{\downarrow})]} + \frac{\lambda^2[\Gamma_{\uparrow} + \Gamma_{\downarrow} + \eta(g_{\uparrow} + g_{\downarrow})]}{2} \right) + 2\lambda^4 J^2}{\eta \lambda^2 g_{\uparrow} \left(\frac{2\epsilon^2}{\lambda^2[\Gamma_{\uparrow} + \Gamma_{\downarrow} + \eta(g_{\uparrow} + g_{\downarrow})]} + \frac{\lambda^2[\Gamma_{\uparrow} + \Gamma_{\downarrow} + \eta(g_{\uparrow} + g_{\downarrow})]}{2} \right) + 2\lambda^4 J^2} \\ &= \lim_{\eta \rightarrow 0} \frac{g_{\downarrow}}{g_{\uparrow}} = \frac{g_{\downarrow}}{g_{\uparrow}}. \end{aligned}$$

Also other results are identical in both our limits, we refer to them in a short-cut way:

$$\begin{aligned} \rho_{11} &= \frac{\Gamma_{\uparrow}^2 g_{\downarrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow})(\Gamma_{\uparrow} g_{\downarrow} + \Gamma_{\downarrow} g_{\uparrow})} & \rho_{22} &= \frac{\Gamma_{\downarrow} \Gamma_{\uparrow} g_{\downarrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow})(\Gamma_{\uparrow} g_{\downarrow} + \Gamma_{\downarrow} g_{\uparrow})} \\ \rho_{33} &= \frac{\Gamma_{\downarrow} \Gamma_{\uparrow} g_{\uparrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow})(\Gamma_{\uparrow} g_{\downarrow} + \Gamma_{\downarrow} g_{\uparrow})} & \rho_{44} &= \frac{\Gamma_{\downarrow}^2 g_{\uparrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow})(\Gamma_{\uparrow} g_{\downarrow} + \Gamma_{\downarrow} g_{\uparrow})} \quad (20) \\ \text{Re } \rho_{23} &= 0 & \text{Im } \rho_{23} &= 0. \end{aligned}$$

If $g_{\uparrow} \neq g_{\downarrow}$, then sharp changes appear in solution (13). Equality between these coefficients was not assumed. We considered the perturbation to be an additional bath-induced channel which points to $g_{\uparrow} \neq g_{\downarrow}$. Rather the standard thermodynamics relation

$$\frac{g_{\downarrow}}{g_{\uparrow}} = \exp \beta \epsilon$$

may be suggested. Derivation of this statement consists in some additional assumptions about the 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. The transfer channel connected with parameter J is in fact also of fourth order, because its direct application to the density matrix (commutator $[J, \rho]$) changes either the ket or bra side of the density matrix only and the comparable process connecting the diagonal terms in the density matrix is thus of fourth order. Then this new included channel is comparably as strong as (in the first interpretation) or even stronger than (in the second argumentation) the first one. We give a twofold 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 impossible for complicated systems. Moreover, this objection also seriously questions the concept of the generalized master equation in general, because treatment of the whole density matrix (of the system) included information about a set of generally incompatible observables. With respect to a particular measurement (here, for example, site occupation probability measurements), the other terms unrelated to this measurement (here off-diagonal matrix elements) always play the role of some kind of memory. So the apparent difference in the treatment of memories is a general property of the formalism as far as incompatible measurements on the system are concerned.
2. Intuition in more complicated cases is uncertain and may fail. One may reinspect the formula (17) 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 now be smaller than the fourth order coherent channel. In fact, the effectiveness of coherent channel transfer is seemingly of a higher order than 4!

4. Indication of instability

We have argued in the previous section that the instability described above is a matter of internal problem of approximation (3). Despite its reasonable behaviour in the time evolution simulation which we proved in appendix A, a problematic step has been indicated above and this problem must be visible purely from the model treatment. In fact, were one not able to give some indication of the instability of the approximation from itself, the situation would have been crucial. First, treatment of formally higher order corrections is not well established in connected theory, and what is worse, it is an extremely difficult task. Furthermore, one could never (in no finite order of calculation) be sure whether the provided approximation is already stable. We discuss two points which are connected with our instability and indicate it.

4.1. Slow decay in spectrum

The simple method enables us to obtain the indication purely from the spectrum of the evolution matrix of kinetic model (3). What is important from a practical point of view, it works without principal difficulties also in complicated models by numerical analysis and, further, an orientational indication can be implemented into a time evolution computer simulation. Only for simplicity and without any change in physical context, we assume that the number of linearly independent eigenvectors is equal to the order of the connected evolution matrix. In particular, in problem (3), this statement is proved, because none of the submatrices has two identical eigenvalues. The general form of the decomposition of a finite (non-normal) matrix is then

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

where ξ_q is the q th eigenvalue and $R_q (L_q)$ is the associated right (left, i.e. usual) row (column) eigenvector. This decomposition holds good the following normalization:

$$\sum_i (R_q)_i (L'_q)_i = \delta_{qq'}$$

Kinetic equations conserve total probability, consequently the eigenvalue 0 is always present. Look at our result in appendix A again. The suspicious eigenvalue is ξ_4 . In perturbation scheme (9), there is a proportionality $\xi_4 \propto \lambda^6$. It is no wonder that this eigenvalue need not be very stable against considering corrections of order $\lambda^4, \eta\lambda^2$. More generally, let us have, in our spectrum, an eigenvalue with real part approaching zero (with $\lambda \rightarrow 0$) and proportional to higher than second power of $\lambda (> 2)$:

$$W_{ij} = 0 \cdot (L_0)_i (R_0)_j + a_1 \lambda^n \cdot (L_1)_i (R_1)_j + \dots$$

We explicitly emphasize that $(L_q), (R_q)$ are also λ dependent, due to which W_{ij} has terms of just the second order.

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

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

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

Of course, not every one of the mathematical ‘perturbations’ is physically interpretable. Some conditions for the evolution matrix stem from the conservation laws (at least particle conservation in the case of solid state physics), etc. Nevertheless, the set of possible perturbations is so large that it surely contains also physically interpretable perturbations. Our model (16) proves such a possibility. In (3), there is the ‘near-the-zero’ eigenvalue proportional to the sixth order in λ , so we could choose the perturbation smaller than we have done. The reciprocal real part of the second smallest eigenvalue (without sign) is connected with the lifetime of relaxation phenomena. Concluding this subsection, we suggest therefore a practical indication of this instability—highly increasing lifetime of decay when the parameter of perturbation is reduced according to the formal scheme of construction of given kinetic equations.

4.2. Analytical treatment of stationary condition

The very simplicity of the particular model (3) enables the analytical treatment of stationary condition (10), which respects unknown processes, described potentially in higher order of the formal theory. This is not a very appropriate method from the 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 rather the further understanding of the origin of the instability for the reader who still has not accepted the presented facts. We need (for simplicity) to assume that there is a unique asymptotical state of the system for our treatment. This is because here we will deal with the stability of the zero eigenvector only. The proof that there is no potential eigenvalue with positive real part (collapse of model) is not provided. Eigenvalues along the imaginary axes with real part so near to zero that it can approach, through some perturbation, the imaginary axis are ignored here as well. We look for a solution of approximation (3) as Taylor series coefficients,

$$\rho = \sum_n \lambda^n \rho^{(n)}.$$

The important difference as compared to the Taylor series of solution (13) is that we explicitly assume the existence of perturbation of order λ^3 , respectively $\eta\lambda^2$, which is otherwise arbitrary. The results which are independent of potential perturbation are only of interest. However, this is a standard correct perturbational method. Such a treatment gives us only a finite number of conditions for Taylor coefficients. The 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

$$\begin{aligned} \rho_{13}^{(0)} = 0 \quad \rho_{24}^{(0)} = 0 \quad \rho_{12}^{(2)} = 0 \quad \rho_{14}^{(2)} = 0 \quad \text{Im } \rho_{23}^{(2)} = 0 \\ \text{Re } \rho_{23}^{(2)} = J(\rho_{33}^{(0)} - \rho_{22}^{(0)}) \quad \rho_{11}^{(0)} = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} \rho_{22}^{(0)} \quad \rho_{44}^{(0)} = \frac{\Gamma_{\downarrow}}{\Gamma_{\uparrow}} \rho_{33}^{(0)}. \end{aligned} \quad (21)$$

The internal problem of the second order approximation (3) becomes clearly apparent. The zeroth order of the density matrix is not resolved by stationary condition (10). We still have a two-dimensional subspace (arbitrary $\rho_{22}^{(0)}, \rho_{33}^{(0)}$) where the steady state can be found. The result (13) is the corollary of the implicit assumption of zero effect of the higher order calculation, not justifiable from the mathematical point of view. One can comprehend that including a potentially higher order perturbation such as (16) will define the zeroth order density matrix in the space of our result (21) with a high degree of arbitrariness.

In contrast, the model (16) is stable against further perturbation. We obtain the additional condition (once, in the order λ^4 or respectively $\eta\lambda^2$)

$$g_{\uparrow} \rho_{22}^{(0)} = g_{\downarrow} \rho_{33}^{(0)}$$

and the zero order of the density matrix is now complete. Therefore, the situation, despite being unpleasant, is not hopeless. One can indicate the instability, and also ways to improve the models in question are possible in principle.

5. The van Hove limit

All our previous results were obtained in a way that, though similar to ordinarily used approximations, is not standard in formal relaxation theory. We introduced perturbational scheme (9) for calculation of the second order kinetic equation for model Hamiltonian (1) and gave some physical arguments for this choice. Nevertheless, the standard variant of great popularity is, of course, the van Hove limit [19, 20]:

$$J \propto 1 \quad \Gamma_{\uparrow}, \Gamma_{\downarrow} \propto \lambda^2. \quad (22)$$

We argue here that the above problem with infinite time asymptotics of the model (1) (in the second order kinetic equation) is sometimes, in particular cases, also reflected in this well

understood limit. To see this we introduce the ‘energetic’ representation in eigenvectors of H_S

$$\mathbf{c}_{\text{II}} = \alpha c_2 - \beta c_3 \quad \mathbf{c}_{\text{III}} = \alpha c_3 + \beta c_2 \quad (23)$$

where

$$\alpha = \frac{\sqrt{2} \left(1 + \sqrt{1 + \frac{4J^2}{\epsilon^2}} \right)}{2 \sqrt{\frac{4J^2}{\epsilon^2} + 1} + \sqrt{\frac{4J^2}{\epsilon^2} + 1}} \propto 1 \quad \beta = \frac{\sqrt{2}J}{\epsilon \sqrt{\frac{4J^2}{\epsilon^2} + 1} + \sqrt{\frac{4J^2}{\epsilon^2} + 1}} \propto \frac{J}{\epsilon}.$$

Hamiltonian (1) now appears:

$$\begin{aligned} H = & \epsilon c_1^\dagger c_1 + \frac{\epsilon}{2} \left(1 + \sqrt{1 + \frac{4J^2}{\epsilon^2}} \right) \mathbf{c}_{\text{III}}^\dagger \mathbf{c}_{\text{III}} + \frac{\epsilon}{2} \left(1 - \sqrt{1 + \frac{4J^2}{\epsilon^2}} \right) \mathbf{c}_{\text{II}}^\dagger \mathbf{c}_{\text{II}} \\ & + \sum_k \left\{ \Omega_k B_k^\dagger B_k + G_k^{(1-2)} (B_k c_1^\dagger (\alpha \mathbf{c}_{\text{II}} + \beta \mathbf{c}_{\text{III}}) + B_k^\dagger (\alpha \mathbf{c}_{\text{II}}^\dagger + \beta \mathbf{c}_{\text{III}}^\dagger) c_1) \right. \\ & \left. + G_k^{(3-4)} (B_k (\alpha \mathbf{c}_{\text{III}}^\dagger - \beta \mathbf{c}_{\text{II}}^\dagger) c_4 + B_k^\dagger c_4^\dagger (\alpha \mathbf{c}_{\text{III}} - \beta \mathbf{c}_{\text{II}})) \right\}. \end{aligned} \quad (24)$$

The levels II and III refer to the so-called bonding antibonding states. There are two bath-induced channels between levels 1, II and III, 4 respectively, in analogy with the previous treatment in the site representation. The difference is that there is no coherent transfer term in the 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).) These channels cause transitions for the short time regime; nevertheless, both 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 such as [7] in the asymptotic region forbids all transitions between pairs of levels 1 + II and of levels III + 4. The asymptotical stationary condition then has two linearly independent solutions.

Nevertheless, $c_1^\dagger c_1 + \mathbf{c}_{\text{II}}^\dagger \mathbf{c}_{\text{II}}$ does not commute with the full Hamiltonian (24), it is not an integral of motion. Consequently, one cannot use the long time (Born–Markov) approximation when looking for time asymptotics—the result may also depend on short time transient effects. The result obtained in this way cannot also formally guarantee the stability of the treatment as above. In appendix B we give the complete second order kinetic equation and its solution in the van Hove scheme. The solution (B6) of stationary condition (10) shows just the same asymptotic state of the density matrix (and potential instability) as (21).

Here we deal with quite a real physical problem: consideration of whether respective levels are isolated and the transfer is strictly forbidden, which suggests the ordinary energy conservation law, or a limited value of electron density can be still transferred, following the fact that the energy conservation law cannot be applied at very short times (virtual processes). In reality, higher order processes can exist of the type of two consequent transitions which must be, however, interpreted as virtual ones. The point is that the energy conservation law then applies between the initial and final states and not for each individual sub-transition that could be, by this law, even formally forbidden (virtual uphill transfers could be connected with just phonon emission). The significance of the van Hove limit excluding such step-like processes is also questioned here.

6. Physical consequences and conclusions

We pointed out an unpleasant consequence of approximative description in kinetic modelling of open systems. We used a particular simple model in order to comprehend the unstable behaviour found recently [1] while discussing some conclusions of earlier papers [16, 17]. In fact we found a paradigmatic situation, which is of wider relevance, and accompanies kinetic modelling in general.

We introduced a four level system whose dynamics was described in correspondence with broadly accepted methods.

The full analysis of the spectrum of the transfer matrix revealed ‘a slow decay to the steady state’ of the sixth order in formal perturbational parameter λ . This and also the formal analytical inspection given in subsection 4.2 connect both particular schemes (18) and (19) together, implying that the above deficiency is a general property of the particular kinetic model. As similar care is not usual in standard modelling, its results could be potentially questioned.

A few words need to be mentioned concerning overcoming the described deficiency. In our particular case, however, there is no simple way to get credible results without either difficult incorporative description of the previously omitted processes following from formally higher order contributions from subsequent exact theoretical concepts, or a subtle work in the construction of the entering Hamiltonian. On the other hand, in many particular cases some conclusions can also be proved [14], whenever some attention is held. Therefore, we insist on careful proofs of the particular results, rather than waste effort in general attempts to overcome the deficiency, irrespective of particular interests and invention of users, or refer to cases that are similar in the author’s opinion.

The present work left out considerations about interesting real physical properties of the introduced model. However, we point out that it embodies some paradigmatic features. It is one of the simplest models considering weak coherent communication between two sites, and the phenomenon of decoherence of comparable strength, connected with channels attached to the dimer. Significant difficulties in establishing kinetics also in the van Hove limit call for interesting investigation, with consequences we do not dare anticipate.

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Appendix A. Detailed analysis of spectrum

Determination of the 12 eigenvalues does not meet with problems, because these are the roots of quadratic polynoms. In addition, we would mainly like to know signs of real parts of the eigenvalues, at least in the limit $\lambda \rightarrow 0$. Thus, we reduce complicated results into the Taylor series at least to the order which gives the sign:

$$\begin{aligned} \xi_1 &= 0 & \xi_2 &= -\Gamma_\uparrow - \Gamma_\downarrow \\ \xi_7 &= -i\frac{\epsilon}{2} - \frac{3\Gamma_\downarrow + \Gamma_\uparrow}{4} + i\sqrt{\frac{\epsilon^2}{4} + i\epsilon\frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4} + J^2} \approx -\Gamma_\downarrow \end{aligned}$$

$$\begin{aligned}
\xi_8 &= -i\frac{\epsilon}{2} - \frac{3\Gamma_\downarrow + \Gamma_\uparrow}{4} - i\sqrt{\frac{\epsilon^2}{4} + i\epsilon\frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4} + J^2} \approx -i\epsilon - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2} \\
\xi_{11} &= -i\frac{\epsilon}{2} - \frac{3\Gamma_\uparrow + \Gamma_\downarrow}{4} + i\sqrt{\frac{\epsilon^2}{4} - i\epsilon\frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4} + J^2} \approx -i\epsilon - \frac{\Gamma_\uparrow + \Gamma_\downarrow}{2} \\
\xi_{12} &= -i\frac{\epsilon}{2} - \frac{3\Gamma_\uparrow + \Gamma_\downarrow}{4} - i\sqrt{\frac{\epsilon^2}{4} - i\epsilon\frac{\Gamma_\downarrow - \Gamma_\uparrow}{4} - \frac{(\Gamma_\downarrow - \Gamma_\uparrow)^2}{4} + J^2} \approx -\Gamma_\uparrow \\
\xi_{15} &= i\epsilon - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2} \\
\xi_9 &= \xi_7^* \quad \xi_{10} = \xi_8^* \quad \xi_{13} = \xi_{11}^* \quad \xi_{14} = \xi_{12}^* \quad \xi_{16} = \xi_{15}^*.
\end{aligned}$$

Further eigenvalues are roots of the fourth order polynomial obtained from the submatrix A. Though there is a formula which enables explicitly to extract the roots—the so-called Cardano formula—we do not use it because of its complicated form, and we only determine leading terms of the limit case $\lambda \rightarrow 0$ 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.)

$$\begin{aligned}
\xi_3 &\approx -\Gamma_\uparrow - \Gamma_\downarrow & \xi_4 &\approx \frac{-J^2(\Gamma_\uparrow + \Gamma_\downarrow)}{\epsilon^2} \\
\xi_5 &\approx i\epsilon - \frac{\Gamma_\uparrow + \Gamma_\downarrow}{2} & \xi_6 &= \xi_5^*.
\end{aligned}$$

Note that the complex square root used in the above formulae is defined in the upper half-plane of the complex plane (e.g. $\text{Im} \sqrt{\cdot} \geq 0$).

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 as follows:

$$\begin{aligned}
\rho^T &= (\rho_{11}, \rho_{\text{II,II}}, \rho_{\text{III,III}}, \rho_{44}, \text{Re } \rho_{\text{II,III}}, \text{Im } \rho_{\text{II,III}}, \text{Re } \rho_{1,\text{II}}, \text{Im } \rho_{1,\text{II}}, \text{Re } \rho_{1,\text{III}}, \\
&\quad \text{Im } \rho_{1,\text{III}}, \text{Re } \rho_{\text{III,4}}, \text{Im } \rho_{\text{III,4}}, \text{Re } \rho_{\text{II,4}}, \text{Im } \rho_{\text{II,4}}, \text{Re } \rho_{14}, \text{Im } \rho_{14}).
\end{aligned}$$

Kinetic equations (2) obtained here from, e.g., [7], are

$$W^{(2)} = \begin{pmatrix} A & 0 & 0 & 0 \\ 0 & B & 0 & 0 \\ 0 & 0 & C & 0 \\ 0 & 0 & 0 & D \end{pmatrix} \quad (\text{B1})$$

where

$$A = \begin{pmatrix} -\Gamma_\downarrow^v & \Gamma_\uparrow^v & 0 & 0 & \theta\Gamma_\uparrow^v & 0 \\ \Gamma_\downarrow^v & -\Gamma_\uparrow^v & 0 & 0 & \theta\Gamma_\downarrow^v & 0 \\ 0 & 0 & -\Gamma_\downarrow^v & \Gamma_\uparrow^v & -\theta\Gamma_\uparrow^v & 0 \\ 0 & 0 & \Gamma_\downarrow^v & -\Gamma_\uparrow^v & -\theta\Gamma_\uparrow^v & 0 \\ \frac{\theta\Gamma_\downarrow^v}{2} & -\frac{\theta\Gamma_\uparrow^v}{2} & \frac{\theta\Gamma_\downarrow^v}{2} & -\frac{\theta\Gamma_\uparrow^v}{2} & -\frac{\Gamma_\uparrow^v + \Gamma_\downarrow^v}{2} & -\epsilon - 2\Delta \\ 0 & 0 & 0 & 0 & \epsilon + 2\Delta & -\frac{\Gamma_\uparrow^v + \Gamma_\downarrow^v}{2} \end{pmatrix} \quad (\text{B2})$$

$$B = \begin{pmatrix} -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} & \epsilon + \Delta & \frac{\theta \Gamma_{\downarrow}^v}{2} & 0 \\ -\epsilon - \Delta & -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} & 0 & \frac{\theta \Gamma_{\uparrow}^v}{2} \\ -\frac{\theta \Gamma_{\downarrow}^v}{2} & 0 & -\Gamma_{\downarrow}^v & -\Delta \\ 0 & -\frac{\theta \Gamma_{\uparrow}^v}{2} & \Delta & -\Gamma_{\downarrow}^v \end{pmatrix} \quad (\text{B3})$$

$$C = \begin{pmatrix} -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} & \epsilon + \Delta & -\frac{\theta \Gamma_{\uparrow}^v}{2} & 0 \\ -\epsilon - \Delta & -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} & 0 & -\frac{\theta \Gamma_{\uparrow}^v}{2} \\ \frac{\theta \Gamma_{\downarrow}^v}{2} & 0 & -\Gamma_{\uparrow}^v & -\Delta \\ 0 & -\frac{\theta \Gamma_{\downarrow}^v}{2} & +\Delta & -\Gamma_{\uparrow}^v \end{pmatrix} \quad D = \begin{pmatrix} -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} & \epsilon \\ -\epsilon & -\frac{\Gamma_{\uparrow}^v + \Gamma_{\downarrow}^v}{2} \end{pmatrix} \quad (\text{B4})$$

where

$$\begin{aligned} \Delta &= \frac{\epsilon}{2} \left(\sqrt{1 + \frac{4J^2}{\epsilon^2}} - 1 \right) \\ \theta &= \frac{\beta}{\alpha} = \frac{2J}{\epsilon \left(1 + \sqrt{1 + \frac{4J^2}{\epsilon^2}} \right)} \\ \Gamma_{\uparrow}^v &= 2\pi\alpha^2 \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon + \Delta - \Omega_k) Tr_{\text{bath}} \rho_{\text{bath}} (B_k^{\dagger} B_k) \\ &= 2\pi\alpha^2 \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon + \Delta - \Omega_k) Tr_{\text{bath}} (\rho_{\text{bath}} B_k^{\dagger} B_k) \\ \Gamma_{\downarrow}^v &= 2\pi\alpha^2 \sum_k [G_k^{(1-2)}]^2 \delta(\epsilon + \Delta - \Omega_k) Tr_{\text{bath}} (\rho_{\text{bath}} B_k B_k^{\dagger}) \\ &= 2\pi\alpha^2 \sum_k [G_k^{(3-4)}]^2 \delta(\epsilon + \Delta - \Omega_k) Tr_{\text{bath}} (\rho_{\text{bath}} B_k B_k^{\dagger}). \end{aligned} \quad (\text{B5})$$

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

$$\rho = C \left(\frac{\Gamma_{\uparrow}^v}{\Gamma_{\downarrow}^v + \Gamma_{\uparrow}^v} c_1^{\dagger} c_1 + \frac{\Gamma_{\downarrow}^v}{\Gamma_{\downarrow}^v + \Gamma_{\uparrow}^v} c_{\text{II}}^{\dagger} c_{\text{II}} \right) + (1 - C) \left(\frac{\Gamma_{\uparrow}^v}{\Gamma_{\downarrow}^v + \Gamma_{\uparrow}^v} c_{\text{III}}^{\dagger} c_{\text{III}} + \frac{\Gamma_{\downarrow}^v}{\Gamma_{\downarrow}^v + \Gamma_{\uparrow}^v} c_4^{\dagger} c_4 \right) \quad (\text{B6})$$

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

This proves the statements of main text.

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