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Particle transfer beyond weak-coupling regime

Evaluation of kinetic method

Ph. D. Thesis

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Preface and Acknowledgements

This thesis was written during the years 1999-2002 at Institute of Physics of Charles University. The subject stemmed from the problem of relation quantum kinetics and thermodynamics which was investigated in Theoretical department by Prof. Čápek from 1997.

The thesis is formed by the introductive part, where the present author describe the background of the work and briefly outlines the conclusions he found and the attached papers, which were published:

1.- F. Šanda, The instability in the long time regime behaviour of a kinetic model
published in: J. Phys. A: Math. & Gen. **35** (2002) 5815.

2.- F. Šanda, The instability in the long time regime behaviour of a kinetic model II
published in: http://arxiv.org/abs/physics/0201040.
Updated version submitted for publication in J. Phys. A: Math. & Gen.

3.- F. Šanda, Note on the equivalence of different approximations in the relaxation theory
published in: Czech. J. Phys. **52** (2002) 729.

The results of the work were presented at Summer School Fundamental Problems in Statistical Physics X in Altenberg (Germany), in August 2001 (poster). The results were also presented at the Faculty Of Mathematics and Physics, Charles University at WDS 2001, and at seminary "Modern Methods of Computer Physics" in November 2002.

I would thank to Professor Vladislav Čápek, who was the supervisor of this thesis. I am indebted to him for suggestion of the theme, brisk discussions on the subject, valuable positive criticism of the papers I wrote, and also lot of help during all the collaboration.

However, I am sorry to say that Professor Čápek deceased shortly before the finish of my Ph. D. anabasis. This thesis is dedicated to his memory.

The great deal of help with computers made also Doc. Jiří Bok. I also thank to all others for discussions or practical help during the years of my Ph.D. study, especially Prof. Ivan Barvík, Prof. Theo M. Nieuwenhuizen. The members of Institute of Physics constituted the hospitable environment for work. Thanks to all of them.

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CONTENTS

ARTICLES

I. INTRODUCTION

A. Background

The second law of thermodynamics constitutes a permanent challenge for a wide spectrum of scientists. Its experimental evidence is of unprecedent robustness, at least in everyday experimental physical experience. Though there are also later, more abstract formulation, given e.g. by Clausius or Carathéodory [1], the second law is usually considered in its different historical formulations by Clausius [2]:
No process is possible, the sole result of which is that the heat is transferred from a body to a hotter one.
or Thomson [3]:
No process is possible, the sole result of which is that a body is cooled and work is done.

However, its very general and ambitious formulations provoke serious questions concerning different areas of its consequences. There were possibly decaying but permanent attempts to break the law directly. Construction of the perpetuum mobile of the second kind (a machine, which can transform heat into usable work without compensation) using the usual technical facilities remains still an area of interest either for enthusiastic laymen, or seriously facing investigations. It is an consequence of the fact that the origin of the second law remains still a bit foggy. However, its unsuccessful history shifted the classical perpetuum mobile off the interest of scientific community.

The main task for theoretical physicists poses the relation between the second law and the constitutive microscopical laws of nature, which are considered to be time reversal. The connected research achieved remarkable successes (see, e.g., [4–6]) and today physicists well understand the way how the microscopically time reversal processes may form the past-future axis, known from our lives, at least for simple paradigmatic cases. However, there is no proof concerning similar consequences in general. Nobody (as far as we know) knows exactly the minimal set of assumptions and definitions that could enable a derivation of second law from microscopical dynamics for all formulations. For instance, the classical formulation of the second law (and the thermodynamics at all) uses the dichotomy system - reservoir. But what are the very conditions to denote some object as a bath? We understand that the bath must be "large". But it seems, that also the condition of a relatively weak system-bath interaction is possibly important, at least for technical purposes. The indefinite role of the van Hove limit [7] is a mirror of this annoyance. Explicitly questioned: Is it necessary for the evidence of canonical asymptotics to consider the van Hove limit, like most of works that prove canonical behavior of particular systems do, or may this condition be omitted what the great experimental evidence in favor of the second law in real, i.e., nonlimit conditions suggests? There is so far no appropriate answer.

The great question in the second law status is its relation to the classical dynamics. As it was stated in the past many times, the dynamics inherently does not distinguish between the past and the future. The constitutively irreversible behavior resulting from the 2-nd law is in the strict opposition to that and the irreversibility is mostly considered as an exception, resulting from very special boundary conditions following the term "set-up of the experiment" inherent to the observer. The second law is then considered as of partially subjective matter. However, such an opinion can hardly be held against attacks of everyday evidence [8, 9]. On the other hand, our comprehension how mechanical dynamics and thermodynamics relates with each other is still incomplete and in fact also the most influential works concerning the subject merely suggest the way for thinking, but do not prove their statements from a microscopical point of view.

Some attention could be focused also to the minority opinion stating that the second law cannot be directly derived from the first principle, but constitute the novel, irreducible, law of nature compatible with but independent of mechanics [8].

Also the necessity of overcoming the thermodynamical view as a forming power to understand the phenomena of living matter were stressed. The role of strongly nonlinear, nonequilibrium processes and their open character is acknowledged. Such a notice changes our opinion about the central position of 2-nd law, but as far as its validity is not questioned, it remains out of our attention.

The scientific history of Maxwell's demon - an intelligent creature or equipment which is owing to his/her excellent cognitive and perceptive abilities and knowledge able to separate hotter and colder molecules - was started by Maxwell and Thomson [10]. Here the demon was considered as principally possible, but impractical being. Emphasis on statistical nature of thermodynamics was the sponsor of his/her birth. The irreversibility was understood here as a tribute for macroscopic manipulations with molecules. Smoluchowski ruled out the case of mechanical equipment inside the system, when he pointed out that it must absorb the heat, what shortly results in demon inability to recognize the state of any particular molecule [11, 12]. (A comprehensive analysis based on Smoluchowski ideas one can find in [13].) Later, Szilard in his famous analysis [14] suggested, that Maxwell demon can work not to owing to but at the cost of his/her knowledge. In the meantime the quantum theory was developed, which supports the opinion that one must pay for knowledge. Szilard work, in fact, widened the previously established connection between thermodynamics and statistical physics also toward theory of information. From that time, a sequence of further analyses concerning the quantum theory followed, that either supported or refused particular Szilard statements (extensive material compiles [15]). Brillouin in [16] provided a price estimation of information acquisition considering a model of molecule - demon communication using photon quanta, that supported Szilard ideas. A number of parallel treatments of different models of information acquisition were developed [17, 18], but the Szilard idea of generally irreversible character of measurement was not uniquely accepted. Also the criticism of the Szilard ideas took place. There are objections against nonphysical status of the demon [19] or fundamental objections against linking thermodynamical entropy (objective, measurable quantity) and subjective, observer-dependent definition of statistical entropy [9]. Further incidence of Szilard work is that [14] did not clearly identify the origin of thermodynamical costs, whether it comes from measurement, remembering or forgetting. This point became clarified by discoveries of Landauer, Bennet, and others that linked the computing process ("information theory") to measurement (physics) [18, 20, 21]. The thermodynamical costs were identified as a consequence of the necessity to erase the memory of the system for cyclization of the process. At this point, the coincidence with the present research becomes apparent [22]. The processes of relaxation are usually considered as spontaneous vanishing of the memory. Of course, the relaxation processes do not steer for the pure state of the system as in [20], rather the opposite is true, but this point need not be the crucial one. A specific form of response of the system to the bath (described standardly by open system Hamiltonian) enables to avoid the presence of any anthropomorphous demon, or manipulations from outside, what elsewhere complicated the analysis. Only standard tools of quantum open system theory are inherent to this research.

B. Generalized master equation

The second latent source of the the present thesis lies in the application of quantum kinetics. In particular application of the so called master equation in open system dynamics treatment is inherent to our investigation. The paradigm of master equation method forms the Pauli master equation introduced in [23]. We omit here other kinetic approaches, e.g., Boltzmann [24] or Focker-Planck equations [25], that also can be related to the master equations, or Green function techniques. Rather we outline the development inspired by the Pauli master equation. The particular progress started at the dawn of sixties, and in the following 20 years the sure-footed fundament of the master equation technique in open system treatment was laid. The first article that touched the subject was a part of an article by Nakajima [26], however, it appeared rather as an accidental fortune than a goal of a systematic development.

The first well founded intentional approach was introduced by Zwanzig [27, 28], who laid down the algebraic fundament of connected kinetics, suggesting the projection technique in the Liouville space. The technique survived in its basic features up today. So called Nakajima -Zwanzig identity forms a background for a wide sort of kinetic models using integro-differential equations called the time-convolution generalized master equations (TC-GME). However, the integro-differential equation is not just the simplest mathematical structure. Therefore attempts appeared soon to integrate the memory terms into time local coefficients. The time convolution-less generalized master equations (TCL-GME) approach was firstly suggested by Fulinski and Kramarczyk [29, 30], and inter-relations with convolution master equations were discussed. The authors pointed out that the dynamics as formulated in fact defines a Markovian process, and they refused to reflect the convolution approach as essentially more exact. Further development consisted mainly in numerous applications of the mentioned approaches in a wide extent of physics. The works of particular importance were [31, 32]. In comparison with previous works where the Zwanzig projection technique extracted, from the complete density matrix of the system, the information concerning populations at some states, here the reduction onto the whole density matrix of the internal system applied while the coherence relations with the bath modes were considered as redundant. Just this type of reduction is today of the greatest popularity and is also inherent to the present thesis.

There is also one next point to be mentioned. Though most of the above fundamental work enunciated the theory in form of exact identities, on some stage, however, any open system treatment must descend to approximations. The master equations formalism already from its beginning was diversified from author to author. Of course, as far as the exact formulas were kept, they were naturally equivalent. However, the necessary introduction of approximative master equations led to suggesting a number of nonequivalent approximations, often without relevant differences in physical motivations. From here a large area for treating properties of particular approximations and relations among them opens [28, 33–36]. An independent direction of development appeared in works by Kubo, Tokuyama, Mori, and others [37–39] who treated alike problems in the Heisenberg picture (i.e. with time evolution own to observables) looking for a quantum generalization of the Langevin equation. Though the applicability of this theory looks often quite differently, also these works were shown to be comprehensible as a special case of the projection technique of the Zwanzig type [33, 40]. Also here, both the time convolution (Mori equation [37]) and the convolutionless (Tokuyama-Mori equation [38]) formulations were used.

Further important progress related to the subject was the mathematical works by E.B.Davies, who suggested a scaling theory, which enabled in many cases to express validity of specified approximations [41–43].

Now we have mentioned the important background sources of investigations and can proceed to introduce the area of problems this thesis concerns.

C. Modified Davies scaling treatment

In the previous six years efforts was underway in the treatment of the open quantum systems that embody some type of self-organized behavior. The main property of investigated systems was a special form of interaction between system and bath, where the bath specifically responds to the position of "observed" species. Some interesting features of behavior were found here. The subject of the greatest controversy was the reported tendency of connected kinetic simulations not steering for the Boltzmann canonical distribution for density matrix in the long time regime. Moreover models could be suggested in a way, where this feature of the simulated behavior was extremely emphasized [44–48]. In fact, the controversy about this evidence happened the dominating subject of discussion concerning behavior of these models.

The treatment was pioneered by Čápek in [49]. The knowledge concerning the subject was extended during the following six years. The issue of connected works can be divided into three groups.

- The first domain gathers the attempts to invent the models simpler, better and more comprehensible. The goal is to find simple models that question foundations of thermodynamics in a direct way, and moreover in an apparent manner. In the sequence of articles [22, 45–52] one may see an apparent progress on this path. Today, by our opinion, the fact is well proved, that simulations constructed as described by Čápek [22, 45, 53] really result into predictions of noncanonical asymtotics. However, similar results were referred also by some independent groups [54–56].

- The second interesting area of the research concerns relation of the achieved results to previously accepted concepts in thermodynamics and statistical physics. We also class to this direction questions whether the treated kinetic models are derivable "ab initio" from the mathematics and first principles of quantum mechanics only, and whether the simulations, regardless the use of quite usual methods only, is not somehow wrong. The immediate question looks for the cornerstone exhibiting difference against the usually assumed Boltzmann asymptotical distribution, that was also referred to be found for simpler models treated using the same formalism (GME) [41]. It was pointed out in [57], that the assumption of the very special system-bath coupling was not the crucial one, rather dropping the weak coupling (van Hove) limit [7] was important. The special form of the system bath coupling was important for exhibiting the noncanonical behavior in a very dramatic way, not like a small deviation, that without physical understanding of its origin would be rather interpreted as a consequence of the imperfectness of model. Later, authors of [53] specified the physical regime of the predicted phenomenon and suggested its formal exhibition in some general modification of scaling technique introduced by Davies [42, 43].

  The interest and view of present author is focused just in this direction probably as a consequence of his theoretical orientation. The main subject of this thesis is a critical inspection of methods and achieved results. In comparison with the previously cited works that are founded by Davies theorems [41–43], the reformulation of the theoretical approach was preferred. We derived the TC-GME using the same perturbational technique, but the errors were not controlled by the scaling techniques. Rather we treated possible influence of higher order contribution more directly. A connection between the formally different approaches is introduced in [58, 59]. In horizon of this Ph.D. thesis, it revealed impossible to give very concluding decision concerning feasibility of the outlined program. The model we are faced with is too complicated for complete analytical solution. However, some further interesting observations were found. The author hopes, that the reader will become deeper interested in such open partial results than in referring further investigation of the first type.

We anticipate shortly our basic observation. We stress serious doubts about stability of asymptotical treatments connected with approximation of the second order in a formal perturbation parameter. Some feature of the referred behavior comes from time scales where the error of the method is not well controlled. Investigations with some relation to our result (i. e. they are concerned with errors of similar type) were also worked out simultaneously [60, 61]. Their result support the need for the care of higher order computation. Therefore, we must insist on the attitude that our result are relevant not only formally. This point is in fact of wide relevancy. **For specified models**, nearly the same arguments may also complicate argumentation in favor of the canonical asymptotics in the van Hove limit. (In some way the importance of the special form of the model returns. Of course, it ensues from the initial stage of the treatment of this specific question, where we need to see the problems sharply.) Reader, who is not interested in theoretical speculations, may read this thesis (at least [59]) also as a set of results of an analytical GME treatment for given open models in a specific physical regime, parallel to [47, 48, 62] and with some additional mathematical care.

- At the end of the introductive part we must finish the counting the area of connected investigations. With sporadic exceptions physicists respect experimental results. High credit of classical thermodynamics does not follow from theoretical speculation, rather the extensive experimental evidence and also that of related scientific branches lie in its grounds. Therefore the third direction of treatment was to try to observe in experiment or Nature some evidences of the referred behavior, and in case of positive answer to comprehend how it can be related to usually observed thermodynamical laws. The set of connected references is as far as we know relatively poor, but not empty, see [56, 63, 64].

II. ON THE PATH OF MOTIVATIONS

The central task of our work was (at least in the first version) the treatment of behavior of one particular quantum open model consisting of particle whose Hilbert space consists of two site, one harmonic oscillator, responding to the location of this particle, and a phonon bath interacting with the oscillator. The full description of the model is in [58], that is a part of this thesis. The model was a logical end of a sequence of models [47, 48, 62], which differ in the number of sites the particle can occupy. Čápek et all [47, 48, 62] found strictly non-canonical infinite time asymptotics and a parallel behavior was also expected to be found here, when the same formal scheme of treatment is held. As a further step, it was planned to add to the model other "bath" modes where the potential of usable work could be stored in form of continual pumping the heat against the temperature step. The present author carefully proved the first step in the plan.

Our task in [58] was to find the asymptotic density matrix of the system containing two sites (the second one polaron shifted) with vibrational levels. The dynamics of the system was driven by a coherent transfer term between the sites and a vibrational relaxation among the excited levels, treated according to modified Davies scaling as suggested by [53]. The specific form of the coherent term was completely analogical to that in previous works [47, 48, 62]. The polaron shift in this case causes the expectation of the non-symmetrical transfer between the sites, what was reported in previous works. This effect was really observed, but serious difficulties appeared in convergence and interpretations of the asymptotic state for some choices of parameters. A careful tracing of the origin of the problems showed that the model contains, aside from the unique asymptotic steady state, also solutions only slowly decaying to zero. This observation was exhibited by investigation of the spectrum of the transfer matrix. The inspection of behavior of this eigenvalue with respect to a formal perturbation parameter of the applied kinetic equation was proved. An eigenvalue was found to approach so near to zero that fall-off of the connected solution is very slow and can not be controlled by mathematics standardly used in kinetic theory. This is the central message of work [58]. Thus, the original task was broken and the subject of treatment was considerably changed. In particular, the applicability of standard kinetic approaches in asymptotical state computation were questioned.

With the first article [58], also a short technical work included into thesis is connected [65]. The general discussion concerning the justification of kinetics treatment is enormously miscellaneous, because in kinetic studies the authors use different formal approaches. Though identities might relate their exact formal version as they describe exactly the same underlying problem, the actually used kinetic models (approximations) differ from each other. [65] amplifies a standard equivalence between the Born approximation of TCL-GME and Born-Markov approximation of TC-GME , known from the van Hove limit and now extended also to a scaling scheme introduced by [53]. However, though such identities have some importance in kinetic modelling we tried to carry out other articles independently of the very specification of used approximations.

Regardless of the identification of a formal deficiency in conventional deductions, the physical relevance of this observation remained foggy. One must consider the frequently observed phenomenon that, in particularly within physics of relaxation, poorly mathematically justified approaches work well. For instance, one should remind of the history of the Fermi golden rule. It was successfully applied in many cases, though some relevant rigorous mathematical theory is known only in some cases like a specific problem of the Auger resonance in atomic spectra [66]. However, so far detailed mathematical study of great part of its applications has not been carried out. Another, more distanced but instructive example is quantum electrodynamics, where the "naive" perturbational finite order theory gave experimentally relevant results though it was from [67] well known that, in fact, the connected perturbation series is divergent.

This situation called for physically comprehensive picture of some simplified parallel system where the found deficiency takes place. The reader can judge how successful the connected effort was by studying work [59]. We restricted the harmonic vibrational mode to two lowest levels. However such a formulation does not differ from reinterpretation as four site system as used in [59]. Thus we treated only a four site system, what enables us to avoid the use of computational power when looking for the asymptotical state. The pairs of sites (e.g. ground state and its excitation) undergo the bath induced relaxation. The coherent transfer between these couples of sites was not directly related to previous work, rather the simplest nonsymmetrical case - the particle at vacuum of site 1 undergoing a transfer to the excited level of the second site a vice versa - was chosen. This system was treated according to [53]. The very simplicity of the model enabled the analytical determination of the asymptotical state within specified approximations and also complete analytical inspection of spectrum of the transfer matrix. The found asymptotics was parallel to that referred by [47, 48, 62]. However, the deficiency referred in [58] was again present.

Furthermore we tried to model the influence of higher order contributions by additional bath-induced transfer between the sites. Considering the limiting process in formal perturbational parameter we found a change in asymptotics, what seriously questions previously obtained results. In addition, we showed how the found instability applies more generally to kinetic models, being not specifically connected only with a special form of the perturbation procedure described in [53], but includes also, and maybe more importantly, many standard approximative approaches and is even present in some pathological cases in the van Hove limit.

III. SUMMARY OF ACHIEVEMENTS

In this section we outline the present situation in the subject concerning developed arguments. We divide the tasks which were raised by [58, 59, 65] into groups -

1, Are the calculations reported in earlier works, related to parallel models, well performed? In particular, is it possible to show directly that the treatment according to the specified method of obtaining kinetic models and modified Davies scaling technique gives the reported results regardless the simplifications used in numerical implementation and without doubts concerning, e.g., numerical errors?

2, How is the usual specifical choice of parameters related to obtained results?

3, How much the specified mathematical theorems really justify the physical conclusions made.

A. Validation of results of the modified Davies scaling

This subsection concerns the issues 1 and 2. The articles below do not discuss this point directly. However, the article [59] indirectly but definitively solves just the task. Section 2 introduces the two site two levels problem which could be related to one sequence of articles as we pointed out above, using just the modified Davies scaling [53]. However, the kinetic model was derived from the Tokuyama-Mori TCL-GME in the second order, therefore we kept exactly the theoretical approach suggested in [53]. In Appendix, the complete resolution of the transfer matrix spectrum in the $\lambda \to 0$ limit was found. In fact, the most important statement is here proved, that for some region of λ parameter surrounding zero, the kinetic model has the unique stationary and asymptotical state. Moreover, in the text, the stationary state is found analytically. It is well related to previously obtained computer simulations and, in particular, in the same way it could be interpreted as "a challenge to standard thermodynamics". However, we pointed out also another possibility - challenging the straightforward applicability of kinetic treatment of the stationary state. Furthermore result of section 2 of [59] also answered the question 2. The obtained asymptotical state is essentially robust with respect to changes of parameter **specified in the kinetic model**. However, from another point of view the results of the mentioned section may serve as a zero point for evaluation of physically relevant properties of the model. Of course, one must on his/her own responsibility accept the relevance of such treatment.

B. Justification of modified Davies scaling treatment

The articles [58, 59] outline the overall result of the stressed task 3, that is of the greatest importance here. As we comment on the particular path where this point first appeared, here we summarize the central message of the articles. We looked the asymptotic density matrix of the two sites + vibration system dynamically completely analogical to [47, 48, 62]. Therefore, the asymmetry of site to site transfer was expected as the consequence of the polaron shift on the one site. Aside from obtaining the parallel asymptotic state the full numerical spectral analysis of the transfer matrix in the long time region was calculated. The evidence of an eigenvalue with very small negative real part was obtained. It implies that there is a solution of the master equation different from the asymptotic one but whose fall off to zero is very slow. Therefore we became interested in behavior of this second smallest eigenvalue while the formal perturbational parameter of theory according to [53] is changed. The result of this treatment one can find in [58]. We found, that this eigenvalue rapidly falls to zero with the perturbation parameter, specifically with the sixth order. As far as the theory comes out from the second order this suggests the idea of a poor stability of such a treatment with respect to processes of formally higher orders in the perturbation theory. Consequently, we turn our attention to Davies theorems, which forms the mathematical background, how is such a case treated. In fact this was a short but at least for us surprising discovery, that these theorems cannot be applied for justifying the asymptotical treatment in our case. The Davies theorems well control the time area up to a time $\propto \lambda^2$, according to its applicability to the second order master equation. But in this time area both the asymptotical and $e^{-\lambda^6 t}$ solutions hardly differ; the referred phenomenon becomes pronounced on the time scale $\propto \lambda^{-6}$, where the errors are not well controlled. We therefore stated and proved, that one can suggest a physically interpretable Markovian evolution which steers for radically different asymptotical state though it fulfils assumptions of the Davies theorems for the same exact (not approximated) Hamiltonian evolution. Further point of investigation consists in a critical scrutiny, what part of the asymptotical results is well justified in our model, and what forms a space of admissible asymptotical states. We found that (in the $\lambda \to 0$ limit) the distribution onto vibrational levels is well founded, but the distribution between sites, which previously referred to the question of the general validity of the canonical asymptotics, is not well justified and consists in belief. The direct identification of a proper asymptotical state necessarily involves calculation in higher orders of the master equation formalism. Unfortunately, this is not well established, and worse it is a very hard task. In the time horizon of this Ph.D.thesis we decided to descend and chose a less ambitious task [59]. We introduce a perturbation of the master equation which is physically comprehensive, and treated it as a contribution of a higher order, though the complete high order inspection were not made. However, what was also pointed out was that the deficiency is not only of mathematical relevance. One can also consider the fact that any model of real nature necessarily includes simplifications. This means that some processes are omitted as irrelevant on grounds of just such insufficient arguments as, e.g., that they are slow or that the relevant coupling constants are small enough.

We pointed out that our work can give also implications for awareness in this direction. This is just the goal of the article [59]. The four site system treated here is related with the previous two site + oscillator provided we restrict the harmonic vibrational mode to two lowest levels. The bath-induced transfer between 1-2 and 3-4 sites and the coherent transfer between 2-3 sites was introduced.

The very simplicity of the model enabled the analytical solution of the asymptotical state within a specified approximation and also a complete analytical inspection of the spectrum of the transfer matrix. Analytical treatment according to the modified Davies scaling procedure [53] found asymptotics parallel to those from [47, 48, 62]. The complete inspection of the full spectrum of the transfer matrix repeated the evidence of an eigenvalue proportional to λ^6. Again the conclusion that is connected with the poor justification of the probability distribution between couples of sites was proved. This point suggested to visualize the facultative influence of formally weaker processes due to attaching a usual bath-induced transfer term between 2-3 sites. The formalization of its small magnitude (as we want to formulate the instability) was carried out in two different ways. The facultative presence of such a term in a formal higher (here the fourth) order was taken into account. Another version consists in amendment of the second order theory with the additional bath-induced channel, but considering it arbitrarily small but nonzero. This implies the challenge to an oversimplified construction of such kinetic models regarding the the overlooked processes in real nature. The investigation showed that in both these cases the influence of new terms completely breaks the asymptotics previously found. The newly established asymptotical distribution between the couple of sites followed the rate ratio of the attached bath-induced transport in the $\lambda \to 0$ limit. Finally in an Appendix, we also showed that the problem can be also related to the better established investigation in the van Hove limit [7], for some pathological cases. Treating the same Hamiltonian using time the convolutionless theory in the van Hove perturbation scheme, one finds that the transition between the couples of sites is (in the second order) forbidden (roughly speaking by the energy conservation law), and so the system has no uniquely given asymptotical state at all. However, the population on the "isolated" subsystems (each pair of sites separately) is not an integral of motion as given by the full Hamiltonian, and in fact there are surely some higher order processes which connect both the subsystems and lie on the energy shell, which broke this "splendid isolation". We conclude this section with short refreshment of the basic statements. We proved in the analytical way that the results of numerical investigations [47, 48, 62] follow from the method specified in [53]. Unfortunately, the sequence of theoretical statements does not form the absolutely closed chain, because the application of the Davies theorems can not formally prove the accuracy of determining of the asymptotical density matrix in our case, however, as well as in many other cases.

IV. (SO FAR) UNJUSTIFIED IDEAS AND PROSPECTS TO FUTURE

The most of our work is focused mainly on technical aspects of mathematical background. so, we would like discuss some of the problems also in physical terms at this place. The reader is recommended not to read this part before studying the published paper.

The relation of the previously achieved results to another formalism used in physics of relaxation is one of the open task. For instance, projection techniques staying in the background of Pauli equation work with the information concerning the population of levels only, without the nondiagonal terms of the density matrix. Therefore one must dispense with the terms decoherence, which lies in the base of argumentation [22]. All the transfers must be expressed in the terms of transfer rates parallel to Fermi Golden rule. However, it is necessary to show that this formalism enables to limit the detailed balance condition, because such a possibility is not known from previously made investigations in the second order perturbation theory.

Another problem is connected with the observation that the coherent transfer is an off-energy-shell process. For compliance with energy conservation law, such process must be succeeded by another virtual processes what is in [22] described by the decoherence effects. It is unlike, that the rates of decoherence, and consequently the "active" process itself, are insensitive with respect to density of phonon modes working on the frequencies of the coherent transfer. In fact in [58] the rate of decoherence is influenced by the density of phonons working on the oscillator energy only. We emphasize, that those two energies do not approach when the perturbational parameter is limited to zero, and can be potentially arbitrarily different. This fact is not something additional to formal arguments given in [58, 59], but provide a physically based argument of the same type, which must be necessarily enlightened.

Some meaningful formal objections can meet also attempts to held the van Hove limit approach for investigations in physical regime specified in [53]. We avoid the informal arguments concerning the personal opinions about the most appropriate form of evolution generator and try to investigate how look like the area where some levels of error of investigation is guaranteed. For instance, we consider the model as described in [58] with $\epsilon \neq 0$ and we are going to discuss the convergence radius of the van Hove type of evolution generator with respect to magnitude J of coherent channel.So, we stay at position

$$J \propto \lambda^0, \quad G \propto \lambda$$

Let us discussed the case $J = 0$ at first. Then, however, the total populations $\sum_\mu c^\dagger_{i,\mu} c_{i,\mu}$ over site $i = 0$ or 1 respectively are integral of motions. The bath induced relaxation is the only channel present here, an consequent resolution of stationary state condition is twofold degenerate. There is some radius of convergence for the strength of bath-system coupling perturbation theory. Whenever $J \neq 0$, one can prove that no further conservative quantity, except the total sum probabilities, does not take place, and the uniquely given asymptotics is expected in the van Hove limit as usually. However, some kind of "singularity" appears also here.

We outline the form of this singularity by an informal physical argumentation. The diagonalization of the H_S now forms "level representation" - bonding and anti-bonding states. Such a state is deviated from the site basis in [58].

$$|0\mu> \rightarrow |0\mu> + J \sum_\nu a_{\mu\nu} |1\nu>$$

The formation of asymptotics is essentially adherent with bonding - antibonding relaxation between which kinetic rate coefficient is of the order $(GJ)^2$. This however naturally implies to keep $G < J$ for applicability of van Hove treatment. Nevertheless, the region of convergence thus vanishing when $J \rightarrow 0$. At the point J=0, as we showed, the character of asymptotical solution dramatically changes. So, the applicability of the van Hove limit fails in the uniform neighborhood of $J = 0, G = 0$. That is, why one cannot easily refuse the interest of the Čápek's scheme of treatment.

However, we avoided also different problems connected with general concept of kinetic method. The usual form of kinetic investigations are far from the rigorous treatment. In particular, the thermodynamic limit of uncountable bath, going with time to infinity and many similar subjects itself and also in relations are often based rather on "physical thinking" than mathematics. Though we are staying fully on the position trust in kinetic methods, doubts can occur concerning the assumption, that evolution toward final state can be described by the kinetic terms as transfer rate etc.

It is very unlike, but in our opinion, the treatment considering the higher order master equations is unavoidable, if the mathematically sounder predications should be obtained.

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