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Zeroth and second laws of thermodynamics simultaneously questioned in the quantum microworld

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Abstract. A new and rather trivial model is suggested with mechanism that implies simultaneous violation of the zeroth and the second laws of thermodynamics. Mathematically rigorous quantum theory reduces to a trivial application of the Golden rule formula. It yields exciton on-energy-shell diffusion caused by bath-nonassisted excitation hopping between tails of different exciton site levels $\epsilon_1 < \epsilon_2$ broadened by bath-assisted finite life-time effects. The elastic character of the hopping implies $1 \leftrightarrow 2$-symmetric transfer rate W. Thus the net diffusion exciton flow $W(P_1 - P_2)$ and also, as argued, the net energy flow are possible due to different near-to-equilibrium exciton populations $P_1 > P_2$. As the sites are provided with two different baths, the population imbalance and the flows survive even for slightly different local bath temperatures $T_1 < T_2 < T_1\epsilon_2/\epsilon_1$. Thus spontaneous exciton and also energy flows against temperature step become possible, in contradiction with the Clausius form of the second law. Violations of both the laws disappear in the high-temperature, *i.e.* classical limit.

PACS. 05.30.-d Quantum statistical mechanics – 05.70.-a Thermodynamics – 44.90.+c Other topics in heat transfer

1 Introduction

Phenomenological arguments against general validity of standard statistical thermodynamics and call for inclusion of cooperative, selforganization and similar complicated phenomena even in absence of, *e.g.*, external flows and far from equilibrium exist already for a long time. Since early nineties, one can find them especially in theory of electron-transfer chemical reactions where, in connection with their phenomenological non-linear description, inclusion of such effects seems to be indispensable [1]. Necessity of their inclusion follows also from detailed analysis of what is known in molecular biology about how individual molecules (molecular machines) work in living organisms [2]. Selforganization is usually believed to be a domain of nonlinear theories. In 1996, the first Hamiltonian linear quantum model was suggested that can lead to a selforganized state upon thermalization in a bath even when no external flows exist and, simultaneously, this state is energetically disadvantageous [3,4]. Recent analysis has revealed that the former non-linear phenomenological and the latter linear first-principle type of reasoning strive in the same direction and can be easily united [5]. The reader is referred to [6–8] or also to [5] for previous models (extending also reasoning of [3,4]) where the cooperative and selforganizational tendencies in such models can be shown to provide a basis and unique possibility of violating even the second law of thermodynamics.

Some of such models allow a mathematically rigorous treatment throughout all the calculations ([6] is perhaps the first one of them). However, for technical reasons, just one-step processes have been treated so far. Only very recently, first in 1998, the first rigorously solvable quantum model working cyclically as a *perpetuum mobile* of the second kind (*i.e.* converting heat from a single bath into, this time, a usable work without compensation) and violating thus, for the first time explicitly, the Thomson formulation of the second law of thermodynamics [9] was reported [10–12]. In 1999 and 2000, also other groups arrived, independently and for other situations, at the same conclusion challenging universal validity of the second law [13–15]. From them, in particular paper [14] by Allahverdyan and Nieuwenhuizen inspired a public response [16]. Completely different mechanism (connected with dynamically maintained steady-state pressure gradients in rarefied gases) potentially allowing violation of the second law was recently suggested by Sheehan – compare, in connection with previous paper [17], the discussion in [18,19]. Another and even rather positively experimentally tested system was suggested by Sheehan already in 1994 [20–22]. Because of complicated nature of the problem as well as owing to 150 years of traditionally presumed universal validity of thermodynamic principles, it is likely that irrespective of final result of the

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above counter-examples, the problem of potential violation of thermodynamic principles will remain topical for many years to come. A comment is only worth mentioning here that the above models of the present group always work from strong correlations (entanglement) among particles and/or competing and mutually interfering reaction (transfer) channels. Thus, like also in [13,14], the mechanisms discussed are appreciably different from those based on, *e.g.*, the Feynman, Ratchet and Pawl systems [23,24]. It is most likely that such ratchet-like systems (that would transform the thermal noise into one-directional linear or rotational motion) rather fail in experiment once they are devised to violate the second law [24], irrespective of previous opposite expectations but fully in accordance with the Feynman original analysis [23].

The above models of the present group (usually described as isothermal Maxwell demon models because of dynamic opening and closing 'gates', *i.e.* reaction channels) are in fact so far sufficiently complicated. Moreover, their classical counterparts do not work. All this is why they can and really do, at the first inspection, naturally induce fully comprehensible prejudice, mistrust, or misunderstandings. To this mistrust, also the fact contributes that the principles on which their activity relies remind of the original Maxwell demon [25] (opening and closing a gate after checking state or performance of previous steps and thus deciding about next elementary steps in, *e.g.*, particle transfer). The idea of Maxwell demon was, however, often and in detail analyzed during the last 130 years [26,27]. Result of the analysis was usually negative but it well applies to just classical models. In this connection, it is worth mentioning that all models [3–8,10–14] really cease to work in the classical (high-temperature) limit. On the other hand, this analysis does not regard purely quantum models working on, *e.g.*, principles known from nature, in particular from the contemporary molecular biology (interplay between particle transfer and accompanying topological reconstruction of the particle surroundings [2]) built in [3–8,10–12].

The situation seems to be even more serious as the quantum model of the isothermal Maxwell demon of [3,4] (model of uni-directional isothermal particle transfer even against potential forces) allows a simple generalization to a greater set of sites available to a greater number of particles. This analysis then implies that in a stationary state (equilibrium one in the sense of thermodynamics), chemical potentials of one sort of particles in two subsystems interconnected by sophisticated (*e.g.* molecular) bridges could become even different [28]. This questions universal validity of another basic principle of the statistical thermodynamics [29]. In order to make the situation simpler, we have here rebuilt the model of [3,4] to describe transfer of excitons (*i.e.* excitation energy) and analyzed principles of its work in connection with those of the original model. It appeared that the rebuilt model could be appreciably simplified to such an extent that it becomes fully independent. No possibility is seen to simplify it further and to preserve, simultaneously, the unusual phenomena investigated. The above elementary steps of 'checking performance of previous steps' and 'opening or closing the gate according to the result of the check', so typical of the Maxwell demon – like models, completely disappeared. What, on the other hand, remained is the existence of quantum interference of different reaction (transfer etc) channels. Except for a small (rather physical than technical) modification connected with presumed initial conditions and existence of two thermodynamic baths, the form of the model is fully standard. Without this modification, its solution is known, has been obtained many times and in many different ways, and is correspondingly believed to be well understood. Also the physics coming out of the complicated mathematics is surprisingly simple: Exciton diffusion due to elastic (on-energy-shell) hopping among tails of exciton levels and to sites with less exciton population. Simplicity of the model and many times verified applicability of the really standard technical 'weaponry' applied to it is what may then, hopefully, change the so far reserved attitude of general public to the above provoking ideas questioning, on grounds of the quantum theory of open systems, universal validity of principles of the statistical thermodynamics. These questioned principles include now, in the light of the present results, not only the second but, as argued below, also the zeroth law of thermodynamics.

2 Model

System of a few levels interacting with a thermodynamic bath is a standard quantum problem. We shall use it also here. Specifically, here, we assume three levels, one ground and two excited ones, and refer to the excited levels as those with a Frenkel exciton placed either on site 1 or site 2. These sites might be, *e.g.*, two different molecules or local centres in, possibly, two different but adjacent solids representing two different electron subsystems. As it is easy to verify, it is for our problem here irrelevant whether we include or ignore the fourth level corresponding to both molecules (molecular systems, local centres) excited. For technical simplicity, we choose the latter alternative. Corrections owing to the (here ignored) two-exciton states are, in, *e.g.*, the excited state occupation probabilities and for small $1 \leftrightarrow 2$ exciton transfer rates, $\propto \exp\{-\beta(\epsilon_1+\epsilon_2)\}$ where ϵ_j, $j = 1, 2$ are the local exciton energies. Thus, they can be easily identified.

The exciton residing possibly at sites 1 or 2 (if not lacking at all for some time owing to finite life-time effects admitted here) can in principle be transferred between the sites (subsystems) either coherently or incoherently. Here, we choose the first alternative, designating the hopping (resonance or transfer) integral as J. Finally, we complete the model by adding a bath interacting with the system. The tricky feature whose real sense will be seen only below is that we ascribe to each subsystem (designated as I with site 1 and II with site 2) its own thermodynamic bath represented by harmonic oscillators (phonons). Because we assume that initially, both the baths have a canonical distribution with possibly equal temperatures, this step is in such a case isomorphic to assuming that the exciton at site 1 or 2 interacts respectively with, *e.g.*, just even or odd modes of a single bath. Technically, the next step is not relevant but physically, it is important to assume that these two baths are in a way separated as we shall discuss the energy (heat) flow from bath I to II and *vice versa*, and we want the exciton mediated channel to be the only one making the heat transfer possible. Adding that the exciton-phonon coupling (with coupling constants g_κ and G_κ) leading to the above exciton finite life-time effects (*i.e.* non-preserving the number of excitons) is assumed linear in the phonon creation ($b^\dagger_{j\kappa}$) and annihilation ($b_{j\kappa}$, $j = 1$ and 2) operators, one can directly write the Hamiltonian as

$$H = H_{\rm I} + H_{\rm II} + J(a_1^\dagger a_2 + a_2^\dagger a_1),$$

$$\begin{aligned} H_{\rm I} &= \epsilon_1 a_1^\dagger a_1 + \sum_\kappa \hbar\omega_\kappa b^\dagger_{1\kappa} b_{1\kappa} \\ &\quad + \frac{1}{\sqrt{N}} \sum_\kappa g_\kappa \hbar\omega_\kappa \left(a_1 + a_1^\dagger\right)\left(b_{1\kappa} + b^\dagger_{1\kappa}\right), \\ H_{\rm II} &= \epsilon_2 a_2^\dagger a_2 + \sum_\kappa \hbar\omega_\kappa b^\dagger_{2\kappa} b_{2\kappa} \\ &\quad + \frac{1}{\sqrt{N}} \sum_\kappa G_\kappa \hbar\omega_\kappa \left(a_2 + a_2^\dagger\right)\left(b_{2\kappa} + b^\dagger_{2\kappa}\right). \end{aligned} \quad (1)$$

The exciton creation (annihilation) operators are assumed to fulfil the Pauli relations

$$\{a_1, a_1^\dagger\} = \{a_2, a_2^\dagger\} = 1, [a_1, a_2^\dagger] = 0,$$

$$\{a_1, a_1\} = \{a_2, a_2\} = [a_1, a_2] = 0 \text{ etc.} \quad (2)$$

Here, $\{\dots, \dots\}$ and $[\dots, \dots]$ are the usual anti- and commutators. The phonon frequencies ω_κ are, for simplicity, assumed the same for both the baths. Finally, ϵ_j, $j = 1$, 2 are the exciton energies while N is the number of the phonon modes (finite before taking the baths thermodynamic limit) in each bath separately. Technically, the existence of two separated and uncorrelated baths, each of them interacting with just one exciton level, makes also the form of our matrices below simpler. One should add here that any two-level system can be represented as a $\frac{1}{2}$-spin, *i.e.* also (1) may be rewritten in terms of two $\frac{1}{2}$-spins s_1 and s_2 interacting here with two separate baths. Unfortunately, for such spin-boson systems [16,30,31], no general exact solution exists. Moreover, the quantity we are here interested in (*e.g.* $\mathrm{I} \propto \Im\mathrm{m}\rho_{12} = \Im\mathrm{m}\langle s_2^+ s_1^- \rangle$ in (26) below) does not belong to those sufficiently investigated in our specific stationary but non-equilibrium (both from the point of view of our system without baths only) time-regime. That is why we start here from the very beginning.

We now want to proceed by writing down a closed set of equations for the exciton density matrix only, projecting off the information about baths. There are several well known ways leading finally to the same result. In order to be specific, we choose time-convolutionless Generalized master equations [32–36] with the Argyres-Kelley projector [37,38]. Practical application of the resulting equations then requires approximations (*e.g.* expansions) upon calculation of coefficients in the equations that can be avoided by application of scaling arguments. The method is well developed and standard now. Describing the formal apparatus, we must be, however, more specific as we are now going to deviate from a standard weak-coupling approach. This is necessary here because of necessity to describe properly interplay between/among several competing processes.

The weak coupling theory was made mathematically perfect by Davies who properly applied the scaling idea of van Hove [39,40]. It is funny to realize that, at least for systems of finite number of levels, the mathematical prescription how to calculate properly the weak-coupling dynamics as provided by the Davies theory is not unique. For that, compare Theorem 1.4 of [40] which establishes full uniqueness just in the full Van Hove limit (see (3) below) but not for arbitrarily weak though finite coupling strengths as it corresponds to reality. Irrespective of it, because of its mathematically rigorous form, this theory (really rigorous in its region of validity) so influenced theoreticians that many of them now consider the weak coupling language as universal. This is, of course, unintentional negative consequence of the mathematical precision of the Davies theory. So, it is also (and even more than above) funny to observe that this theory fails to describe, *e.g.*, the physical regime we are here interested in. This is owing to the overestimation, in the Davies (or, more generally, weak coupling) theory, of the role of in-phasing (that is, in our case, owing to, *e.g.*, the coherent exciton transfer $1 \leftrightarrow 2$) as compared to the standard dephasing[1]. The latter dephasing process is, in our case, simply due to the exciton (electron) coupling to the bath. Let us be even more specific:

The standard weak-coupling theory is based on the notion of a small parameter, say g, of the coupling of the system to the bath. This means that g would be a joint small parameter of the last terms on the right hand sides of $H_{\rm I}$ and $H_{\rm II}$ in (1) only. Then a new unit of time, say $\tau = t/t'$ is chosen and we work, instead of the true physical time t, in terms of the dimensionless time t'. Avoiding here technical details how to avoid Poincaré cycles by performing first the thermodynamic limit of the bath [41], the result is that finally, the proper weak-coupling equations for the exciton density matrix are obtained (otherwise as below) by taking the combined limiting Van Hove procedure

$$g \to 0, \ \tau \to +\infty, \ g^2\tau = \text{const.} \quad (3)$$

Omitting at this moment also less important mathematical details (see [40,42]), the statement is that the resulting equations then describe properly the time development of the system, in terms of the new time t', to its canonical state corresponding to the (initial) temperature of the

[1] This overestimation is not owing to any formal error, it is because of the very form of the presumed Van Hove scaling. In Nature, there is, *e.g.*, no possibility to scale coupling constants as they are real constants, not variables.

bath. Because of the limit $g \to 0$ incorporated into (3) and because the coherent (transfer or hopping) integrals responsible for the in-phasing are kept finite during this limit, the role of the dephasing processes in competing the in-phasing ones is fully suppressed. This is why the corresponding asymptotic, *i.e.* canonical density matrix is then diagonal in the basis of the eigenstates of the Hamiltonian of the system $H_{\rm S}$ alone. In other words, this is why the relaxation goes to eigenstates of $H_{\rm S}$.

In order to incorporate the above and in Nature really existing competition between dephasing and in-phasing processes, we shall proceed in almost the same way except for one point: We take g as a small parameter of not only the system coupling to the bath. We also assume that $J \propto g^2$. The resulting limiting procedure is thus not that of the weak coupling but that of, rather, slow transfer processes. Concerning the relative strength of the $1 \leftrightarrow 2$ transfer and relaxation owing to the coupling to the bath, it might be, in such a scheme and for a general situation, still arbitrary. Here, we shall, however, assume that the latter coupling is rather intermediate or even strong as compared to the coherent $1 \leftrightarrow 2$ transfer of the exciton in the sense that the dephasing is either comparable to, or even dominates over in-phasing. (Concerning the words '...dominates over...' remember, that in the situation of the weak coupling case, the in-phasing is, in the limiting sense of (3), *infinitely* stronger than the dephasing. Here, on the contrary, we admit in our case of the intermediate or strong coupling that the dephasing could be even dominating over the in-phasing but, figuratively speaking, their ratio remains always *finite* though perhaps arbitrarily large.) This causes remarkable differences in structure of the equations we aim at as well as in the physical conclusions. In particular, we then get that the relaxation does not go (in the sense of diagonalizing the asymptotic density matrix) to the eigenstates of the Hamiltonian of the system. To what state (*i.e.* to what exciton density matrix) the relaxation then goes we shall see later.

Technically, the method of deriving the closed set of equations for the exciton density matrix proceeds in the following steps:

- We introduce the density matrix of the 'system+bath(s)' complex in the 'interaction' picture as

$$\tilde{\rho}(t) = \exp\{{\rm i}\mathcal{L}_0\, t\}\rho_{\rm S+B}(t). \tag{4}$$

  Here $\rho_{\rm S+B}(t)$ is the density matrix of the system and the bath in the Schrödinger picture and the Liouvillean $\mathcal{L}_0 \ldots = [H_0, \ldots]/\hbar$ where, however, $H_0 = \sum_{j=1}^{2}[\epsilon_j a_j^\dagger a_j + \sum_\kappa \hbar\omega_\kappa b_{j\kappa}^\dagger b_{j\kappa}]$. In other words, the hopping term $J(a_1^\dagger a_2 + a_2^\dagger a_1)$ is now *not* included in H_0. This is unlike the scaling inherent to the weak-coupling case (3).
- We apply, *e.g.*, the Fuliński and Kramarczyk identity [32,33], or its more famous form by Shibata, Hashitsume *et al.* [34,35]

$$\begin{aligned}\frac{\rm d}{{\rm d}t}\mathcal{P}\tilde{\rho}(t) = &-{\rm i}\mathcal{P}\mathcal{L}(t)\left[1 + {\rm i}\int_0^t \exp_{\leftarrow}\right.\\ &\times\left\{-{\rm i}\int_{\tau_1}^t (1-\mathcal{P})\mathcal{L}(\tau_2)\,{\rm d}\tau_2\right\}\\ &\left.\times(1-\mathcal{P})\mathcal{L}(\tau_1)\exp_{\rightarrow}\left\{i\int_{\tau 1}^t \mathcal{L}(\tau_2)\,{\rm d}\tau_2\right\}{\rm d}\tau_1\right]^{-1}\\ &\times\left[\exp_{\leftarrow}\left\{-{\rm i}\int_0^t (1-\mathcal{P})\}\mathcal{L}(\tau)\,{\rm d}\tau\right\}(1-\mathcal{P})\rho(0)+\mathcal{P}\tilde{\rho}(t)\right].\end{aligned} \tag{5}$$

  (For equivalence of (5) with [32,33] see [36].) Here $\mathcal{P}$ is the so called Argyres-Kelley projector [37,38]

$$\mathcal{P}\ldots = \rho^{\rm B}\,{\rm Tr}_{\rm B}(\ldots), \tag{6}$$

$$\mathcal{L}(t)\ldots = \exp\{{\rm i}\mathcal{L}_0\, t\}\frac{1}{\hbar}[\tilde{H}, \ldots]\exp\{-{\rm i}\mathcal{L}_0\, t\}, \tag{7}$$

  and

$$\begin{aligned}\tilde{H} = J\left(a_1^\dagger a_2 + a_2^\dagger a_1\right) + \frac{1}{\sqrt{N}}\sum_\kappa \hbar\omega_\kappa\left[g_\kappa\left(a_1 + a_1^\dagger\right)\right.\\ \left.\times\left(b_{1\kappa} + b_{1\kappa}^\dagger\right) + G_\kappa\left(a_2 + a_2^\dagger\right)\left(b_{2\kappa} + b_{2\kappa}^\dagger\right)\right].\end{aligned} \tag{8}$$

- Assume, for simplicity, initially factorizable density matrix of the exciton and bath and identify $\rho^{\rm B}$ with the initial density matrix of the bath.
- Perform the above scaling (including transition to new time t' – we shall, however, continue writing t) with also $J \propto g^2$,
- Return back from the above 'interaction' picture to the Schrödinger picture.

(Details of this procedure may be found, for similar models, elsewhere – see, *e.g.*, [43] for a method fully following the Davies approach [40,42].) Then, after some straightforward algebra, the required set of equations for the density matrix of the exciton only (designated as $\rho(t)$), that is exact in the sense of the above scaling procedure, reads

$$\frac{\rm d}{{\rm d}t}\begin{pmatrix}\rho_{00}(t)\\ \rho_{11}(t)\\ \rho_{22}(t)\\ \rho_{12}(t)\\ \rho_{21}(t)\end{pmatrix} = \begin{pmatrix}\mathcal{A} & \mathcal{B}\\ \mathcal{C} & \mathcal{D}\end{pmatrix}\cdot\begin{pmatrix}\rho_{00}(t)\\ \rho_{11}(t)\\ \rho_{22}(t)\\ \rho_{12}(t)\\ \rho_{21}(t)\end{pmatrix}. \tag{9}$$

Here the blocks

See equation (10) in next page.

From the whole set of 9 equations for elements $\rho_{ij}(t)$, $i, j = 0, 1$ or 2, we have in (9) omitted those ones that are separated (the whole set factorizes) and are not important below. Index 0 corresponds to the unexcited state where there is no exciton in the system. As for, *e.g.*, the

$$\mathcal{A}=\begin{pmatrix}-\gamma_\uparrow-\Gamma_\uparrow & \gamma_\downarrow & \Gamma_\downarrow\\ \gamma_\uparrow & -\gamma_\downarrow & 0\\ \Gamma_\uparrow & 0 & -\Gamma_\downarrow\end{pmatrix},\ \mathcal{B}=\begin{pmatrix}0 & 0\\ \mathrm{i}J/\hbar & -\mathrm{i}J/\hbar\\ -\mathrm{i}J/\hbar & \mathrm{i}J/\hbar\end{pmatrix},\ \mathcal{C}=\begin{pmatrix}0 & \mathrm{i}J/\hbar & -\mathrm{i}J/\hbar\\ 0 & -\mathrm{i}J/\hbar & \mathrm{i}J/\hbar\end{pmatrix},$$

$$\mathcal{D}=\begin{pmatrix}-\frac{1}{2}(\gamma_\downarrow+\Gamma_\downarrow)+\mathrm{i}(\epsilon_2-\epsilon_1)/\hbar & 0\\ 0 & -\frac{1}{2}(\gamma_\downarrow+\Gamma_\downarrow)-\mathrm{i}(\epsilon_2-\epsilon_1)/\hbar\end{pmatrix}. \quad (10)$$

zero elements in the $\mathcal{D}$ matrix, these are owing (and correspond) to the above stressed importance of the existence of two baths. This also makes a difference between two Davies schemes (see [40]) irrelevant here. The following notation has been used:

$$\begin{aligned}\gamma_\uparrow&=\frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa (g_\kappa\hbar\omega_\kappa)^2\frac{1}{\exp(\beta_1\hbar\omega_\kappa)-1}\delta(\hbar\omega_\kappa-\epsilon_1),\\ \gamma_\downarrow&=\frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa (g_\kappa\hbar\omega_\kappa)^2\left[1+\frac{1}{\exp(\beta_1\hbar\omega_\kappa)-1}\right]\delta(\hbar\omega_\kappa-\epsilon_1),\\ \Gamma_\uparrow&=\frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa (G_\kappa\hbar\omega_\kappa)^2\frac{1}{\exp(\beta_2\hbar\omega_\kappa)-1}\delta(\hbar\omega_\kappa-\epsilon_2),\\ \Gamma_\downarrow&=\frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa (G_\kappa\hbar\omega_\kappa)^2\left[1+\frac{1}{\exp(\beta_2\hbar\omega_\kappa)-1}\right]\delta(\hbar\omega_\kappa-\epsilon_2).\end{aligned} \quad (11)$$

Implicitly, we assume everywhere the thermodynamic limit of the bath(s) to be already performed. As for β_1 and β_2, notice that we have assumed the bath to consist of two (sub-)baths designated as 1 and 2, each of them connected with its own subsystem I or II (forming inherent part thereof). In order to get rid of the inhomogeneous initial condition terms (otherwise resulting in the set (9)), we have assumed that the bath is initially statistically independent of the system. We impose further condition here: As the two sub-baths do not directly interact, we ascribe both of them initial canonical distributions with presumably different initial temperatures T_1 and T_2. Then $\beta_j=1/(k_\mathrm{B}T_j)$, $j=1,\ 2$. All derivation here and below applies for even $T_1\neq T_2$. Unless the opposite is mentioned explicitly below, however, we can for simplicity assume the two initial temperatures of the baths equal, *i.e.* $\beta_1=\beta_2\equiv\beta=1/(k_\mathrm{B}T)$. Then only one type of the Bose-Einstein distribution $n_\mathrm{B}(z)=[\exp(\beta z)-1]^{-1}$ for phonons enters the above formulae. Worth mentioning here is also the fact that all the γ's and Γ's in (11) result as standard Golden Rule transition rates (fulfilling the usual detailed balance conditions) between states of a localized and absent exciton. No J appears in these formulae. Also this is one of consequences of our above scaling procedure that leads to description of relaxation not in the weak-coupling but rather intermediate or strong coupling regimes (comparable dephasing which is due to the coupling to the bath, and in-phasing which is owing to the above J-term (hopping term)). There is no approximation here.

3 Relation to the weak-coupling limit dynamics

The weak-coupling limit dynamics is best described in terms of eigenstates of the Hamiltonian of the system split off the bath

$$H_\mathrm{S}=\sum_{j=1}^{2}\epsilon_j a_j^\dagger a_j+J(a_1^\dagger a_2+a_2^\dagger a_1). \quad (12)$$

In our case, one such an eigenstate is known, it is the ground state $|0\rangle$ of the electronic system (no exciton in the system). Assume henceforth that $\epsilon_1\neq\epsilon_2$. Then the next two eigenstates states read

$$|+\rangle=\chi|1\rangle-\phi|2\rangle,\ |-\rangle=\phi|1\rangle+\chi|2\rangle \quad (13)$$

where

$$\begin{aligned}\phi&=\frac{2J\mathrm{sign}(\epsilon_2-\epsilon_1)}{\sqrt{2\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}\left[|\epsilon_2-\epsilon_1|+\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}\right]}},\\ \chi&=\sqrt{1-\phi^2}\\ &=\frac{|\epsilon_2-\epsilon_1|+\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}}{\sqrt{2\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}\left[|\epsilon_2-\epsilon_1|+\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}\right]}}.\end{aligned} \quad (14)$$

The corresponding eigenenergies (unperturbed by the coupling to the bath) read

$$E_\pm=\frac{1}{2}[\epsilon_1+\epsilon_2\mp\mathrm{sign}(\epsilon_2-\epsilon_1)\sqrt{(\epsilon_2-\epsilon_1)^2+4J^2}]. \quad (15)$$

Clearly $|+\rangle\to|1\rangle$ and $|-\rangle\to|2\rangle$ when $J\to 0$. In the basis of states $|0\rangle$, $|+\rangle$, and $|-\rangle$, the rigorous weak-coupling dynamics [39,40] as obtained by scaling (3) of the exciton density matrix with the above initial condition reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\rho_{00}(t)\\ \rho_{++}(t)\\ \rho_{--}(t)\\ \rho_{0+}(t)\\ \rho_{+0}(t)\\ \rho_{0-}(t)\\ \rho_{-0}(t)\\ \rho_{+-}(t)\\ \rho_{-+}(t)\end{pmatrix} = \begin{pmatrix}\dots & \dots & \dots\\ \dots & \mathcal{EN}-\mathcal{DIF} & \dots\\ \dots & \dots & \dots\end{pmatrix}\cdot\begin{pmatrix}\rho_{00}(t)\\ \rho_{++}(t)\\ \rho_{--}(t)\\ \rho_{0+}(t)\\ \rho_{+0}(t)\\ \rho_{0-}(t)\\ \rho_{-0}(t)\\ \rho_{+-}(t)\\ \rho_{-+}(t)\end{pmatrix}$$

$$+\begin{pmatrix}-\gamma_{+0}-\Gamma_{-0} & \gamma_{0+} & \Gamma_{0-} & 0 & 0 & 0 & 0 & 0 & 0\\ \gamma_{+0} & -\gamma_{0+} & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ \Gamma_{-0} & 0 & -\Gamma_{0-} & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & k & p & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & p & k^* & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & l & q & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & q & l^* & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & m & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & m^*\end{pmatrix}\cdot\begin{pmatrix}\rho_{00}(t)\\ \rho_{++}(t)\\ \rho_{--}(t)\\ \rho_{0+}(t)\\ \rho_{+0}(t)\\ \rho_{0-}(t)\\ \rho_{-0}(t)\\ \rho_{+-}(t)\\ \rho_{-+}(t)\end{pmatrix}. \tag{16}$$

Here

$$\gamma_{+0} = \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa \left(\chi^2 g_\kappa^2 + \phi^2 G_\kappa^2\right)(\hbar\omega_\kappa)^2 n_{\mathrm{B}}(\hbar\omega_\kappa) \times \delta(E_+ - \hbar\omega_\kappa),$$

$$\gamma_{0+} = \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa \left(\chi^2 g_\kappa^2 + \phi^2 G_\kappa^2\right)(\hbar\omega_\kappa)^2 [1 + n_{\mathrm{B}}(\hbar\omega_\kappa)] \times \delta(E_+ - \hbar\omega_\kappa),$$

$$\Gamma_{-0} = \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa \left(\phi^2 g_\kappa^2 + \chi^2 G_\kappa^2\right)(\hbar\omega_\kappa)^2 n_{\mathrm{B}}(\hbar\omega_\kappa) \times \delta(E_- - \hbar\omega_\kappa),$$

$$\Gamma_{0-} = \frac{2\pi}{\hbar}\frac{1}{N}\sum_\kappa \left(\phi^2 g_\kappa^2 + \chi^2 G_\kappa^2\right)(\hbar\omega_\kappa)^2 \times [1 + n_{\mathrm{B}}(\hbar\omega_\kappa)]\delta(E_- - \hbar\omega_\kappa), \tag{17}$$

are the Golden Rule transfer rates between eigenstates of the unperturbed Hamiltonian of the system H_{S}; clearly, *e.g.* $\gamma_{+0} \to \gamma_\uparrow$ when $J \to 0$ etc. Further, $\begin{pmatrix}\dots & \dots & \dots\\ \dots & \mathcal{EN}-\mathcal{DIF} & \dots\\ \dots & \dots & \dots\end{pmatrix}$ is the 9×9 diagonal matrix with diagonal elements 0, 0, 0, $\frac{\mathrm{i}}{\hbar}E_+$, $-\frac{\mathrm{i}}{\hbar}E_+$, $\frac{\mathrm{i}}{\hbar}E_-$, $-\frac{\mathrm{i}}{\hbar}E_-$, $\frac{\mathrm{i}}{\hbar}(E_- - E_+)$, and $\frac{\mathrm{i}}{\hbar}(E_+ - E_-)$. Finally,

$$k = -0.5(\gamma_{+0}+\gamma_{0+}+\Gamma_{-0}),\quad l = -0.5(\Gamma_{-0}+\Gamma_{0-}+\gamma_{+0}),\quad m = -0.5(\gamma_{0+}+\Gamma_{0-}),\quad p = 0.5(\gamma_{+0}+\gamma_{0+}),\quad q = 0.5(\Gamma_{0-}+\Gamma_{-0}). \tag{18}$$

Topologically, the weak-coupling relaxation matrix (the square matrix in the second term on the right hand side of (16)) resembles that in our intermediate or strong-coupling case (9–10). These relaxation matrices are written down in different bases, however, and in these bases, they have a simple, standard and easily understandable form. Difference between the 'extended' basis $|0\rangle$, $|+\rangle$, and $|-\rangle$ and the 'localized' one $|0\rangle$, $|1\rangle$, and $|2\rangle$ is why the free-motion terms (the first terms on the right hand side of (16) and (9)) formally differ. Coincidence of the free-motion terms is of course complete once they are brought to the same (either localized or extended) basis. This is, on the other hand, unlike the relaxation matrix. If we set $J \to 0$ in all the coefficients in the relaxation matrix in the extended basis in the second term in (16), we do *not* reproduce the relaxation matrix of (9) in this basis. Instead, we get, in this way, the relaxation matrix of (9) as it is written down in (9), *i.e.* in the localized basis. The point is that

- in the scaling (3) underlying the weak-coupling regime, the in-phasing (which is due to J that is kept *constant* during the scaling) is automatically, as a consequence of (3), presumed *dominating* over dephasing processes. Nothing is changed on this feature even if we additionally take J arbitrarily small. That is why the free-motion term is diagonal in the extended basis and the relaxation term describes relaxation in the same basis, *i.e.* that of eigenstates of H_{S} with $J \neq 0$. This relaxation including dephasing is, owing to the form of (3), to be understood as (in the limiting sense) infinitely slow as compared to the in-phasing processes. On the other hand,
- with our scaling

$$g \to 0,\ J \to 0,\ \tau \to +\infty,\ g^2\tau = \mathrm{const},\ \frac{g^2}{J} = \mathrm{const}., \tag{19}$$

  also J is scaled. Hence, as we are allowed, in such a scaling, to keep just second order (in g) processes, we must set $J = 0$ inside all the relaxation superoperator (correction to $\mathcal{PL}(t)\mathcal{P}\rho(t)$ on the right hand side of (5)) as the latter is already $\propto g^2$ owing to its proportionality to the second power of the coupling to the bath). That is why the relaxation term in (9) describes relaxation to eigenstates of $H_{\mathrm{S}}|_{J=0}$, *i.e.* in the localized basis. J must be, however, kept nonzero in the free-motion term. That is why we get a proper competition between free-motion (no transitions in the extended basis, *i.e.* between eigenstates of $H_{\mathrm{S}}|_{J\neq 0}$) reflecting in-phasing owing to term $\propto J$ in (1), and relaxation going between eigenstates of $H_{\mathrm{S}}|_{J=0}$, *i.e.* in the localized basis.

The situation in our intermediate or strong coupling case connected with scaling (19) thus reminds a bit of the Hubbard model when the band and site-local interaction terms are diagonal just in the extended and local bases, respectively. In our case, full equivalence between (16) and (9) appears only in the extreme case of J taken as zero from the very beginning, in both the free-motion and relaxation terms. This is because then the extended and localized bases coincide.

4 Particle and energy flows

Let us return to our above scheme of the slow exciton dynamics as described by (9–10) and let us first discuss solution for the case of zero J (for this particular case, correspondence with the weak-coupling approach as above can be found quite easily). It is easy to verify that the stationary (and in this particular case definitely also equilibrium) solution to (9) reads

$$\rho_{00} \equiv \rho_{00}(t \to +\infty) = 1 - \rho_{11} - \rho_{22},\ \rho_{11} = \frac{\exp(-\beta\epsilon_1)}{Z},$$
$$\rho_{22} = \frac{\exp(-\beta\epsilon_2)}{Z},\ Z = 1 + \exp(-\beta\epsilon_1) + \exp(-\beta\epsilon_2). \tag{20}$$

As for stationary values of site off-diagonal elements of ρ, they turn to zero. So as to derive (20), we have used the detailed balance relations $\gamma_\uparrow/\gamma_\downarrow = \exp(-\beta\epsilon_1)$ and $\Gamma_\uparrow/\Gamma_\downarrow = \exp(-\beta\epsilon_2)$. Formulae (20) are still in full agreement with the equilibrium statistical mechanics, in particular the canonical distribution. In order to see that, let us realize that we have omitted, for purely technical reasons, the two-exciton state with both levels (1 and 2) occupied by excitons. This means errors of the order $\propto \exp(-\beta(\epsilon_1 + \epsilon_2))$. Within this accuracy, we can well approximate, *e.g.*, the stationary value ρ_{11} as $\rho_{11} \approx \frac{\exp(-\beta\epsilon_1)}{1+\exp(-\beta\epsilon_1)}$ what is the canonical equilibrium probability P_1 of finding the site 1 occupied by the exciton, as prescribed by the equilibrium statistical mechanics. Refraining, on the other hand, for a while from the above omission of the two-exciton state and designating the two-exciton state as state 3, we might reconsider the problem on the more general level. This would yield the stationary value $\rho_{11} = \exp(-\beta\epsilon_1)/Z'$ and $\rho_{33} = \exp(-\beta(\epsilon_1+\epsilon_2))/Z'$ where $Z' = Z + \exp(-\beta(\epsilon_1 + \epsilon_2))$. From that, the probability of finding the exciton at site 1 irrespective of the occupation of site 2 results as $P_1 \equiv \rho_{11} + \rho_{33} = \frac{1}{1+\exp(\beta\epsilon_1)}$ [2], in a full correspondence with the above reasoning based on discussion of accuracy of our treatment.

Interesting and important for what follows below is also the dynamics of occupation of site 1. As we still keep $J = 0$, we may for this purpose ignore the state 2 at all. Doing so, we shall for a while completely neglect $\gamma_\uparrow$ as compared to $\gamma_\downarrow$[3]. Then the dynamics (time dependence) of probability of finding the exciton at site 1 reads

$$P_1(t) = P_1(t = 0)\mathrm{e}^{-\gamma_\downarrow t}. \tag{21}$$

This corresponds to the probability amplitude of finding the exciton at site 1 in form of $\mathrm{e}^{-\mathrm{i}\epsilon t/\hbar-\gamma_\downarrow t/2}$ whose Fourier transform reads as Lorentzian $\frac{1}{\pi}\frac{\gamma_\downarrow/2}{[\omega-\epsilon_1/\hbar]^2+[\gamma_\downarrow/2]^2}$. This indicates that the exciton level ϵ_1 (and similarly for the level ϵ_2) is broadened as a Lorentzian with the half-width$\gamma_\downarrow/2$ ($\Gamma_\downarrow/2$). This is what we shall need below.

All this is very reasonable and known, in different context, for already many years. In what follows, we return to a general situation. We shall argue now that the matter will drastically change once we put J nonzero though there is no non-analycity at $J = 0$ here. To be more concrete, we are now going to argue that under the above defined conditions and for, *e.g.*, equal initial temperatures of the baths $T_1 = T_2 = T$, there will be a permanent exciton (and also energy) J-dependent flow between sites 1 and 2. Because of our joining these sites with different and mutually non-interacting baths, this will imply also existence of the energy flow also between our whole subsystems I and II.

This prediction is perhaps shocking for standardly thinking physicists. In order to make the situation physically more clear, let us admit two important things right here:

- The weak-coupling theory does not yield the persistent nonzero flows.
- Application of the canonical distribution to the whole system (consisting of two subsystems, each of them having its own bath and electronic, *i.e.*, exciton levels) also yields that these flows are in average zero.

The counter-arguments against such an easy beating off our type of reasoning and results are, however, as follows:

- The weak coupling theory has even potentially no possibility to yield such flows at all. So, it cannot serve as an arbitrator. The point is that such flows, as shown below, need a sufficiently strong dephasing (as compared with in-phasing processes) to broaden the energy levels ϵ_1 and ϵ_2 (as we shall see below, the transfer is between tails of these levels). The very definition of the weak-coupling approach (see (3) above) is based on the Van Hove limit leading to a negligible role of the dephasing (as compared to the in-phasing), *i.e.* with negligible level broadening. Thus, such approach is in principle unable to model the situation with flows we speak about[4]. Under the condition of the dominating in-phasing (over the dephasing as in the weak-coupling regime), the exciton at sites 1 and 2 also becomes shared. In other words, a special type of a covalent bonding appears between the sites which (as also found in other situations) prevents such flows.
- If we are really right in our prediction that, in the thermodynamic limit, there is a persistent flow between sites 1 and 2, *i.e.* between systems I and II, application of the canonical distribution is unjustified. The point is that the canonical distribution is based on maximizing entropy under solely two constraints: Normalization condition ($\mathrm{Tr}\,\rho = 1$) and mean energy

[2] This is the standard Fermi-Dirac distribution for excitons that behave as paulions, *i.e* on-site fermions, with zero value of their chemical potential.

[3] It is always $\gamma_\uparrow/\gamma_\downarrow = \exp(-\beta\epsilon_1)$ (the detailed balance condition). This ratio is definitely $\ll 1$ for $k_{\mathrm{B}}T \ll \epsilon_1$. On the other hand, except in (21), this condition is not used below.

[4] Notice also that, for, *e.g.*, negligible relativistic corrections and in absence of external magnetic field, the canonical density matrix is real in our local basis $|1\rangle$ and $|2\rangle$. Hence, formula (26) below yields zero flow between sites 1 and 2 in the canonical equilibrium, irrespective of the Golden-Rule-type prediction (31).

conservation ($\mathrm{Tr}(H\rho) = \bar{E} = \text{const.}$). If we are right, then at least the third constraint $\mathrm{Tr}(\hat{I}\rho) = \text{const.}$ ($\hat{I}$ being the flow operator) should be added what makes the usual canonical distribution improper. Also other approaches used to justify the canonical distribution always use, explicitly or implicitly, the *ad hoc* assumption of non-existence of other persistent quantities than energy. So, if we are really right in our arguments here, then, definitely, nor the canonical distribution can be used as an arbiter.

In order to confirm the existence of the stationary flows, let us start our reasoning here by deriving a sufficiently reliable form of the exciton flow formula. From our Hamiltonian (1) and the Liouville equation, we get that

$$-\frac{\mathrm{d}}{\mathrm{d}t}\langle a_1^\dagger a_1\rangle = \frac{\mathrm{i}}{\hbar}\langle [a_1^\dagger a_1, H]\rangle = \frac{2J}{\hbar}\Im\mathrm{m}\langle a_2^\dagger a_1\rangle + \frac{2}{\sqrt{N}}\sum_\kappa g_\kappa\omega_\kappa \Im\mathrm{m}\langle b_{1\kappa}^\dagger a_1\rangle \cdot \quad (22)$$

The last mean value can be calculated, using principle of the adiabatic switching on the interactions, as

$$\delta\langle b_{1\kappa}^\dagger a_1\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle b_{1\kappa}^\dagger a_1\rangle = -\frac{\mathrm{i}}{\hbar}\langle [b_{1\kappa}^\dagger a_1, H]\rangle,\ \delta \to 0+. \quad (23)$$

Here, terms containing J should already be omitted if we work to the second order in our small parameter g only (remember that $J \propto g^2$ – see (19)). Thus, within this accuracy,

$$\langle b_{1\kappa}^\dagger a_1\rangle \approx \frac{1}{\hbar\omega_\kappa - \epsilon_1 + \mathrm{i}\hbar\delta}\frac{1}{\sqrt{N}}g_\kappa\hbar\omega_\kappa \times \Big\{n_{\mathrm{B}}(\hbar\omega_\kappa)[1-\langle a_1^\dagger a_1\rangle] - [1+n_{\mathrm{B}}(\hbar\omega_\kappa)]\langle a_1^\dagger a_1\rangle\Big\} \cdot \quad (24)$$

So, because $\langle a_n^\dagger a_m\rangle = \rho_{mn}$, (22) reads within the required accuracy as

$$-\frac{\mathrm{d}}{\mathrm{d}t}\langle a_1^\dagger a_1\rangle \approx \frac{2J}{\hbar}\Im\mathrm{m}\rho_{12} - \rho_{00}\gamma_\uparrow + \rho_{11}\gamma_\downarrow. \quad (25)$$

As the last two terms express the exciton number imbalancing owing to transfers $1 \leftrightarrow 0$, the proper formula for the real $1 \leftrightarrow 2$ flow is connected with the first term on the right hand side of (25). Thus, the $1 \leftrightarrow 2$ exciton flow (taken as positive if flowing from 1 to 2) reads

$$I = \frac{2J}{\hbar}\Im\mathrm{m}\rho_{12}. \quad (26)$$

The fact that I is determined by the (imaginary part of the) site off-diagonal elements of the particle density matrix follows already from the elementary quantum mechanics ((26) also has a direct connection to standard quantum mechanical formula $I \propto \Psi^*\cdot\nabla\Psi - \nabla\Psi^*\cdot\Psi$).

The long-time (stationary) value of the ρ_{12} element of the density matrix can be found, however, from (9) (by setting the time-derivatives zero), incorporating also the normalization condition

$$\sum_{j=0}^{2}\rho_{jj} = 1. \quad (27)$$

After a simple algebra, the result is

$$I = \frac{2\pi}{\hbar}J^2\frac{1}{\pi}\frac{\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)}{[\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)]^2 + [\epsilon_2 - \epsilon_1]^2} \times \frac{\gamma_\uparrow\Gamma_\downarrow - \gamma_\downarrow\Gamma_\uparrow}{\gamma_\downarrow\Gamma_\downarrow + \gamma_\downarrow\Gamma_\uparrow + \gamma_\uparrow\Gamma_\downarrow + X[\gamma_\downarrow + \Gamma_\downarrow + 2\gamma_\uparrow + 2\Gamma_\uparrow]} \neq 0. \quad (28)$$

Here

$$X = \frac{2\pi}{\hbar}J^2\frac{1}{\pi}\frac{\frac{\hbar}{2}(\gamma_\downarrow + \Gamma\downarrow)}{[\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)]^2 + [\epsilon_2 - \epsilon_1]^2} \cdot \quad (29)$$

Since we are obliged to stick to the required accuracy, we should deal, using the formalism allowed, with just the leading terms. Hence, we shall omit the terms $\propto X$ in the denominator assuming that

$$X \ll \frac{\gamma_\downarrow\Gamma_\downarrow}{\gamma_\downarrow + \Gamma_\downarrow} \cdot \quad (30)$$

This assumption physically means limitation to a regime of so small values of J that the intersite exciton transfer still does not appreciably influence near-to-equilibrium exciton site occupation probabilities. In (28) it implies that, up to terms of higher than sixth order in g (still remember that $J \propto g^2$),

$$I \approx \frac{2\pi}{\hbar}J^2\frac{1}{\pi}\frac{\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)}{[\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)]^2 + [\epsilon_2 - \epsilon_1]^2} \times \frac{\gamma_\uparrow\Gamma_\downarrow - \gamma_\downarrow\Gamma_\uparrow}{\gamma_\downarrow\Gamma_\downarrow + \gamma_\downarrow\Gamma_\uparrow + \gamma_\uparrow\Gamma_\downarrow} = \frac{2\pi}{\hbar}J^2\frac{1}{\pi}\frac{\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)}{[\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)]^2 + [\epsilon_2 - \epsilon_1]^2}[\rho_{11} - \rho_{22}]. \quad (31)$$

Interesting point is that the expression for the exciton flow on the right hand side of (31) is correct even without assuming (30). This follows from (28) by taking into account that from (9), we obtain the asymptotic-time populations

$$\rho_{11} = \frac{\gamma_\uparrow\Gamma_\downarrow + X(\gamma_\uparrow + \Gamma_\uparrow)}{\gamma_\downarrow\Gamma_\downarrow + \gamma_\downarrow\Gamma_\uparrow + \gamma_\uparrow\Gamma_\downarrow + X(\gamma_\downarrow + \Gamma_\downarrow + 2\gamma_\uparrow + 2\Gamma_\uparrow)} \approx \frac{\mathrm{e}^{-\beta\epsilon_1}}{Z},$$

$$\rho_{22} = \frac{\gamma_\downarrow\Gamma_\uparrow + X(\gamma_\uparrow + \Gamma_\uparrow)}{\gamma_\downarrow\Gamma_\downarrow + \gamma_\downarrow\Gamma_\uparrow + \gamma_\uparrow\Gamma_\downarrow + X(\gamma_\downarrow + \Gamma_\downarrow + 2\gamma_\uparrow + 2\Gamma_\uparrow)} \approx \frac{\mathrm{e}^{-\beta\epsilon_2}}{Z} \cdot \quad (32)$$

In the last approximate expressions, we have again used condition (30).

Clearly, expression (31) for the exciton flow is, quite surprisingly at the first sight, clearly nonzero. Already this is remarkable as we have to realize again that the exciton transfers energy and the transfer channel 1↔2 is the only channel connecting our systems I and II and able, within our model, to transfer thus energy between them. Before getting into more physical details connected with this observation, let us also comment that expression (31)

- has a proper total balance structure with transitions $1 \to 2$ and $2 \to 1$ (contributing to (31) by terms $\propto \rho_{11}$ and $\propto \rho_{22}$, respectively), and
- is fully compatible with (in fact, it is exactly equal to) the second-order Golden Rule of quantum mechanics (J is the matrix element of the transfer part of the Hamiltonian between states of the exciton at sites 1 and 2) with the fact incorporated that the energy conservation law should be, in a consistent way like above, properly broadened owing to exciton decay processes. For potential critics of the above approach, let us mention that this form of the Golden Rule formula is fully standard, was many times properly derived and always found sound. Any doubts concerning our above approach would thus inevitably mean questioning of the Golden Rule. For the special case of only one bath, it is nothing but, *e.g.*, formula (6.8.27) of [44].

The broadening in (31) means that the exciton transfer is neither at level ϵ_1 nor at level $\epsilon_2 (\neq \epsilon_1)$ but generally at arbitrary energy in tails of the two broadened exciton levels. (Realize that the exciton is, as generally in nature and as also anticipated in our model, just a finite life-time quasiparticle.) This interpretation is clearly confirmed by the fact that one can rewrite (31) also as

$$I = \frac{2\pi}{\hbar} J^2 [\rho_{11} - \rho_{22}] \times \int_{-\infty}^{+\infty} \frac{1}{\pi} \frac{\frac{\hbar}{2}\gamma_\downarrow}{[\frac{\hbar}{2}\gamma_\downarrow]^2 + [\epsilon - \epsilon_1]^2} \frac{1}{\pi} \frac{\frac{\hbar}{2}\Gamma_\downarrow}{[\frac{\hbar}{2}\Gamma_\downarrow]^2 + [\epsilon - \epsilon_2]^2} \,\mathrm{d}\epsilon \tag{33}$$

and the fact that any quasiparticle exponentially damped with the decay rate γ, *i.e.* the survival probability amplitude

$$\langle a_1(t) a_1^\dagger \rangle = \exp(-\mathrm{i}\epsilon_1 \, t/\hbar - \gamma t/2), \tag{34}$$

has its energy level (here ϵ_1) broadened into a Lorentzian with the energy half-with $\hbar\gamma/2$. See also a comment in this respect above. The forms of (31) and (33) thus leave only very limited space for speculations about validity of our approach.

Our results (31) and (33) imply existence of the net exciton flow in one direction but still not exactly anything about energy (heat) flow. The point is that the net exciton flow consists of forth and back flows which could take place at different levels in the overlap region of the tails of the broadened exciton levels on the energy axis. So let us raise the question what is the proper formula for the energy flow between the two subsystems. According to the above quasiparticle interpretation, one would expect that the energy flow is

$$\begin{aligned} Q &= \frac{2\pi}{\hbar} J^2 [\rho_{11} - \rho_{22}] \\ &\quad \times \int_{-\infty}^{+\infty} \frac{1}{\pi} \frac{\frac{\hbar}{2}\gamma_\downarrow}{[\frac{\hbar}{2}\gamma_\downarrow]^2 + [\epsilon - \epsilon_1]^2} \frac{1}{\pi} \frac{\frac{\hbar}{2}\Gamma_\downarrow}{[\frac{\hbar}{2}\Gamma_\downarrow]^2 + [\epsilon - \epsilon_2]^2} \,\epsilon \,\mathrm{d}\epsilon \\ &= \frac{2\pi}{\hbar} J^2 [\rho_{11} - \rho_{22}] \frac{\hbar}{2\pi} \frac{\epsilon_2\gamma_\downarrow + \epsilon_1\Gamma_\downarrow}{[\frac{\hbar}{2}(\gamma_\downarrow + \Gamma_\downarrow)]^2 + [\epsilon_2 - \epsilon_1]^2}. \end{aligned} \tag{35}$$

The problem is with general justification of this formula. In fact, one should define the energy flow Q between systems I and II in full generality as

$$Q = -\frac{\mathrm{d}}{\mathrm{d}t} \langle \bar{H}_I \rangle \tag{36}$$

or equivalently

$$Q = \frac{\mathrm{d}}{\mathrm{d}t} \langle \bar{H}_{II} \rangle \,. \tag{37}$$

Here $\bar{H}_{\mathrm{I}}$ and $\bar{H}_{\mathrm{II}}$ should have the meaning of energies of the subsystems I and II, such, that $\bar{H}_{\mathrm{I}} + \bar{H}_{\mathrm{II}} = H$ (in order to have (36) compatible with (37)). (Attempts to define Q *via* energy contents of just baths I and II finally yield, in view of finite heat capacity of our finite exciton system and in the stationary situation, the same result.) Because J must be assumed nonzero, these evidently cannot be the Hamiltonians H_{I} and H_{II} introduced in (1). Really, making this or any other trivial identification of $\bar{H}_{\mathrm{I}}$ and $\bar{H}_{\mathrm{II}}$ leads to hardly interpretable results. The physical reason for that is that nonzero values of J cause effects like J-dependent renormalization of the exciton coupling to the bath. Its exact form is unknown so that one can ignore it only when the corresponding coupling constants are negligibly small (when there is practically nothing to be renormalized). That is why, for very small g_κ (*i.e.* negligible $\gamma_\downarrow$), one can define the energy flow properly and reliably by (36), identifying (in this particular case) $\bar{H}_{\mathrm{I}}$ with H_{I}. Then, after completely the same type of algebra as above, (36) reduces to the above formula (35) with negligible $\gamma_\downarrow$. In the opposite limiting case, when G_κ gets very small (*i.e.* with negligible $\Gamma_\downarrow$), (37) also reduces to the above formula (35), this time with negligible $\Gamma_\downarrow$, provided we identify $\bar{H}_{\mathrm{II}}$ with H_{II}.

So summarizing:

- Suggested interpolation formula for the energy flow (35) can thus be properly justified in at least the two above mentioned limiting cases. Then it definitely yields generally nonzero values of the energy flow between our subsystems when $\epsilon_1 \neq \epsilon_2$ and still $T_1 = T_2$ (equal initial temperatures of the two baths) or even $T_1 \neq T_2$, always in the direction from the system with higher near-to-local-equilibrium exciton population to that one with the lower population. Exception is when $T_1\epsilon_2 = T_2\epsilon_1$ when the site populations $P_1 \equiv \rho_{11}$ and $P_2 \equiv \rho_{22}$ would become equal.
- Formula for the exciton flow (31), or its equivalent form (33), can be, in the above way and in contrast to

(35), properly justified for *all* the values of the parameters involved. It always, for $\epsilon_1 \neq \epsilon_2$ and $T_1 = T_2$ (or $T_1 \neq T_2$ but $T_1\epsilon_2 \neq T_2\epsilon_1$), yields nonzero exciton flow between the subsystems, again in the direction from the system with higher (to that one with the lower) near-to-local-equilibrium population P_j of the corresponding exciton level. As the excitons bear energy, this clearly explains why (35) could imply nonzero mean energy flow as obtained above.

In particular, assume now that, *e.g.*, $\epsilon_2 > \epsilon_1$. Assume also that $T_2 > T_1$ but so that still $T_2 < T_1\epsilon_2/\epsilon_1$ applies. Then clearly long-time (near-to-local-equilibrium) site-occupation probability ρ_{11} is still greater than that of site 2, *i.e.* ρ_{22}. This means that $Q > 0$ implying that our spontaneous net energy flow goes in the direction from site 1 to site 2, *i.e.* against temperature step. This conclusion is of highest importance.

5 How long can such flows survive

One should always warn the reader that scaling methods apply to arbitrarily long but still finite rescaled times. In this sense see the book by Davies [39] and the mathematical form of his final statements. Thus, as usual, the formalism used here *can* be applied to the stationary situation obtained, after some initial transient period following establishing the contact between our subsystems I and II, when difference of stationary exciton site populations begins to cause the nonzero flows as above. On the other hand, one *cannot* say, on grounds of the scaling formalism *for general relaxing systems* only, what happens afterwards.

Fortunately, physical arguments help appreciably in our specific case. The point is that in contrast to most of the relaxation problems solved so far, we have two baths with initially different temperatures that are, after their thermodynamic limit (as performed above), already infinite. Thus, their heat contents becomes thus also infinite and relative changes of their heat contents caused by the finite heat flow between them are consequently, after any finite time interval, definitely zero. We cannot say what is the state of the baths in such a stationary situation with nonzero flows – our formalism projecting off the baths does not allow that. Anyway, we definitely know that, *e.g.*, average energy per one bath mode (whose number grows, in the thermodynamic limit, to infinity) thus remains time-independent, keeping bath-I and bath-II temperatures (or whatever else replacing these notions) constant and, for initially $T_1 \neq T_2$, permanently different. So, fully surprisingly from the point of view of standard relaxation problems but necessarily as dictated by the existence of two infinite baths in our situation, our flows should survive forever. Hence, the question 'what happens afterwards' is, *in our specific model*, likely meaningless.

In practice with macroscopic but finite bodies, however, the situation is different. The flows may survive for just a finite time but finally, they necessarily disappear. What is then the form of the density matrix of the complex 'system+baths' remains uncertain. Definitely, however, the reduced density matrix of the system only cannot be canonical. As a general formalism of the equilibrium statistical mechanics shows, it becomes canonical just in the zeroth order in the system-bath interaction. One should notice that in this order, the energy broadening disappears, *i.e.* the physical mechanism making, at finite times, the above persistent flows possible disappears, too. That would mean to return to standard physics.

6 Towards the second law of thermodynamics

There are several formulations of the second law. The form by Clausius from 1865 involves entropy that was not discussed here. Existence of entropy is, however, in fact consequence of three main formulations of the second law, that one by Thomson (1849), Clausius (1850), and Carathéodory (1909) (for connections to entropy see [9] or standard textbooks on axiomatic thermodynamics). The statements are (cited according to [9]):

Thomson (as Lord Kelvin of Largs since 1892) [45]: *No process is possible, the sole result of which is that a body is cooled and work is done.*

Clausius [46]: *No process is possible the sole result of which is that the heat is transferred from a body to a hotter one.*

Carathéodory [47]: *In any neighbourhood of any state there are states that cannot be reached from it by an adiabatic process.*

The words 'sole' imply in particular that

- in the Thomson formulation, the process should be cyclic, without any compensation (additional heat transfer to another and cooler body). A (thought) machine working in such a style is often called 'perpetuum mobile of the second kind';
- in the Clausius formulation, the process is not aided from outside.

Significance of this law and consequences of its potential violation were perhaps best described in the Introduction of [9]. For 150 years, nobody really questioned this statement based on uncountable number of observations from our everyday life. One should add and stress therefore that our above system governed by quantum mechanics and comprising macroscopic baths is macroscopic, *i.e.* it should obey the Clausius (and not only this) formulation of the second law *provided* that the quantum mechanics and thermodynamics are always, including the quantum- and at least the macro-world, compatible. However, the opposite is true: The specific interaction between our two *macroscopic* baths mediated by our *microscopic* exciton system implies existence of the persistent and spontaneous energy and heat flows. Really transferred heat can easily become macroscopic as it is proportional to the time interval used. Hence, owing to specific but standard features of our *microscopic* exciton system, the above reported nonzero values of Q going against the temperature step explicitly contradict the Clausius formulation of the second law of the *macroscopic* thermodynamics.

Sometimes, absolutistic statements in favour of the unconditional validity the second law in the macroworld stemming from our everyday experience appear ("...No exception to the second law of thermodynamics has ever been found – not even a tiny one..." [48]). Let us mention, however, that in the last time, genuine experimental challenges to this law start to appear [20,22,17,13,19]. Also theoretical challenges exist – see the Introduction and the conclusions above. The situation is even more serious as the mechanism reported here is based on just a simple diffusion and its (here again derived) characteristics that have been, in general systems, experimentally verified many times before. One should also mention here the 'pawl and ratchet' systems originally suggested by Feynman [23] which are also often cited in connection with the second law. These systems, however, so far fail in practical attempts to violate the second law [24], in full agreement with the Feynman [23] theoretical analysis. On the contrary, behaviour of the above model as obtained from the rigorous quantum theory of open systems without any uncontrollable step does, as argued above, contradict the second law. As compared to other theoretical challenges – see, *e.g.*, [11,8] and papers cited above or therein – the present model is, on the other hand, perhaps the simplest one. Worth mentioning is also that the above criteria for the energy flow against the temperature step may easily be compatible with, *e.g.*, even room or higher temperatures. In the infinite temperature (*i.e.* in the classical) limit, however, the effect disappears.

7 Towards the zeroth law of thermodynamics

In order to be specific, let us state what this law (so often, especially in the mechanical context, understood as trivial) says: *If system A is in equilibrium with systems B and C then B is in equilibrium with C* (see, *e.g.*, [49]). It helps to introduce thermodynamic temperature, chemical potential etc. Though *universal* validity of this law has already been questioned (as far as its form for equality of chemical potential of one sort of species in different phases in equilibrium is concerned) – see [28] or in the implicit form in [4], no special attention has so far been paid to this fact. That is why we should address the question, in connection with our model above, again.

Let us fix, in the above model, again the situation with $\epsilon_1 < \epsilon_2$ and be T_1 arbitrary positive. Then clearly site-occupation probabilities equal at the second-bath temperature $T_2 = T_2^{\rm crit} \equiv T_1\epsilon_2/\epsilon_1 > T_1$. Hence, upon establishing then a contact between subsystems I and II by taking J slightly (in the sense of (30)) nonzero, we get no energy or exciton flow. Now, we can invoke standard thermodynamic definition of what it means to say that two bodies in a contact are in mutual equilibrium. The definition reads that introducing arbitrary obstacles hindering flows between the bodies does not change their thermodynamic state. In this sense, this is exactly the situation we are now in: We have two bodies in a contact where there are no flows between them. Hence, the thermodynamic state cannot be violated by any obstacle setting these flows zero and not influencing otherwise the state of the systems because the flows are already zero. (Notice that also no other flows but those of exciton or energy can exist in our model.) Remind, on the other hand, that we have such a strange thermodynamic equilibrium (in the above thermodynamic sense) that temperatures of both the systems (those of their baths) are different. This can clearly lead to other contradictions with the standard thermodynamics as we are now going to show.

Assume now that we have still another (third) exciton level and still another (third) thermal bath attached to it. In other words, we complement our Hamiltonian by terms

$$\begin{aligned}\Delta H = \epsilon_3 a_3^\dagger a_3 + \sum_\kappa \hbar\omega_\kappa b_{3\kappa}^\dagger b_{3\kappa} \\ + \frac{1}{\sqrt{N}}\sum_\kappa h_\kappa \hbar\omega_\kappa \left(a_3 + a_3^\dagger\right)\left(b_{3\kappa} + b_{3\kappa}^\dagger\right) \\ + \frac{1}{\sqrt{N}}\sum_\kappa H_\kappa \hbar\omega_\kappa \left(a_2^\dagger a_3 + a_3^\dagger a_2\right)\left(b_{2\kappa} + b_{3\kappa} + b_{2\kappa}^\dagger + b_{3\kappa}^\dagger\right) \\ + K\left(a_3^\dagger a_1 + a_1^\dagger a_3\right). \quad (38)\end{aligned}$$

Clearly, the last two terms on the right hand side of (38) provide interaction of subsystems II and III (this type of the phonon-assisted interaction exists just in the diabatic (non-rigid) basis [50]) and that of the subsystems III and I (the latter interaction and the induced exciton transfer is for simplicity assumed coherent, like that one of the subsystems I and II). Assume also that the exciton energy ϵ_3 equals to that of the exciton in subsystem I, *i.e.* $\epsilon_3 = \epsilon_1$. Next, we assume that again, the initial density matrix is factorizable into a product of density matrices of all the subsystems, so that there are no exciton-bath initial statistical correlations between any two of the three subsystems. Finally, assume that the density matrices of all the baths are initially canonical. Corresponding temperatures are assumed as $T_3 = T_2 > T_1$ (the last inequality being assumed already above).

Let us for a while set $J = K = 0$. Then we have our subsystem I fully separated and the dynamics goes between subsystems II and III only. Exactly in the same way as above (*i.e.* using the same type of scaling), we get a closed set of equations for the matrix elements of the exciton system. This time, however, the situation is simpler as compared to that above. First, our coupling between subsystems II and III is assumed as bath-assisted. In connection with that, the set of equations for the site diagonal as well as site off-diagonal matrix elements of the exciton density matrix factorizes so that equations comprising the diagonal elements contain *only the diagonal* elements (that get separated from the set for the off-diagonal elements), reducing in form to the Pauli master equations [51]. Properties of these equations are sufficiently known. So we shall not repeat the calculations and refer the interested reader to any elementary textbook of kinetic theory. The result for the asymptotic exciton occupation probabilities reads as in the standard equilibrium statistical thermodynamics, *i.e.*

$$\rho_{22} = \frac{\exp(-\beta_2\epsilon_2)}{1+\exp(-\beta_2\epsilon_2)+\exp(-\beta_2\epsilon_1)},$$

$$\rho_{33} = \frac{\exp(-\beta_2\epsilon_1)}{1+\exp(-\beta_2\epsilon_2)+\exp(-\beta_2\epsilon_1)},\ \beta_2 = \frac{1}{k_\mathrm{B}T_2}\cdot \quad (39)$$

Let us stress the following points:

- Values (39) properly reproduce, within our approximation (omission of multi-exciton states, *i.e.* with errors $\propto \exp(-\beta_2(\epsilon_2+\epsilon_1))$), standard equilibrium statistical mean exciton numbers at sites 2 and 3, *i.e.* $1/[\exp(\beta_2\epsilon_2)+1]$ and $1/[\exp(\beta_2\epsilon_1)+1]$ (see a comment above concerning appearance of these Fermi-Dirac distributions for excitons). In fact, as already argued above, reintroducing the multiple-exciton states would reproduce these values exactly. These Fermi-Dirac distributions are, on the other hand, proper mean number of excitons at sites 2 and 3 for $H_\kappa = 0$, *i.e.* separated subsystems II and III. Hence, establishing or cancelling the above contact between the latter two subsystems does not change the stationary (equilibrium) exciton populations at the corresponding sites. The same may be shown to apply to phonon populations in the corresponding baths.
- Assume now $H_\kappa \neq 0$. Owing to the incoherent (bath-assisted) character of the above coupling between subsystems II and III, different populations of levels 2 and 3 (in accordance with standard statistical thermodynamics) do not contradict the fact that (exciton mediated) flows between subsystems II and III remain in equilibrium exactly zero. This is due to the fact that real $2 \to 3$ and $3 \to 2$ transition rates are proportional to $\rho_{22} \times \{1 + 1/[\exp(\beta_2\hbar\omega_\kappa) - 1]\}$ and $\rho_{33} \times 1/[\exp(\beta_2\hbar\omega_\kappa) - 1]\}$, respectively. Here, by the energy conservation law, $\hbar\omega_\kappa = \epsilon_2 - \epsilon_1 > 0$. The multiplicative factors at ρ_{22} and ρ_{33} are phonon statistical factors describing phonon-assisted induced as well as spontaneous processes. So, the transfer rates $2 \to 3$ and $3 \to 2$ are in equilibrium exactly equal, mutually cancelling their contribution to the exciton as well as energy flow between subsystems II and III (transferred energy is $\epsilon_1 + \hbar\omega_\kappa = \epsilon_2$). Here, for simplicity, we have assumed (in accordance with assumptions underlying validity of the Pauli equations) that $|\epsilon_2 - \epsilon_3|/\hbar \equiv |\epsilon_2 - \epsilon_1|/\hbar$ is appreciably greater than the sum of broadenings of levels 2 and 3, *i.e.* that the transitions are practically (exciton+phonon) energy conserving. These arguments are what underlies the detailed balance conditions in the Pauli master equation theories yielding the same conclusion.

These are the characteristics of the mutual equilibrium (according to the above thermodynamic definition) state of subsystems II and III, and also of the internal equilibrium states of the isolated subsystems II and III taken separately. With this states, let us now put $H_\kappa = 0$ (we split subsystems II and III), keep $J = 0$ but put $K \neq 0$. Let us repeat: We have the two subsystems (I and III) with equal exciton energies $\epsilon_1 = \epsilon_3$ (this case may be treated as a limit $\epsilon_1 - \epsilon_3 \to 0$ in the above formulae), initially in internally canonical states of both the subsystems (and their baths), with the respective temperatures $T_1 < T_2 = T_3$. In accordance with what has been said above about development of two such subsystems (previously subsystems I and II above) with their respective baths, the asymptotic (stationary) populations of the exciton levels 1 and 3 only slightly change upon establishing contact between the subsystems as far as K remains sufficiently small. Asymptotically, they read

$$\begin{aligned}\rho_{11} &= \frac{\exp(-\beta_1\epsilon_1)}{1+\exp(-\beta_1\epsilon_1)+\exp(-\beta_2\epsilon_1)} \approx \exp(-\beta_1\epsilon_1),\\ \rho_{33} &= \frac{\exp(-\beta_2\epsilon_1)}{1+\exp(-\beta_1\epsilon_1)+\exp(-\beta_2\epsilon_1)} \approx \exp(-\beta_2\epsilon_1),\\ \beta_1 &= \frac{1}{k_B T_1}\cdot\end{aligned} \quad (40)$$

Clearly, because $\beta_2 < \beta_1$, the populations ρ_{11} and ρ_{22} are different. So, according to (31), (33) as well as (35), there are flows between the subsystems I and III, *i.e.* we have no equilibrium in the thermodynamic sense.

Thus, summarizing, we have subsystems I, II and III which all have well defined temperatures. Upon establishing just the above specific contact between I and II, the systems stay, in the sense of the thermodynamic definition, in equilibrium. Similarly, upon establishing just the above contact between subsystems II and III, the thermodynamic equilibrium is not violated. All three systems (together with their baths) are macroscopic. Thus, the zeroth law of thermodynamics should be, according to thermodynamics, well applicable. It states that establishing contact between subsystems I and III should preserve their mutual equilibrium state. As seen above, however, *the opposite is true.*

8 Conclusions

We have investigated one standard and rather trivial model that allows rigorous treatment by methods of the quantum theory of open systems. The obtained behaviour contradicts what is prescribed by the second as well as zeroth laws of thermodynamics. In connection with previously expressed doubts about universal validity of the second law in specific situations, this extends challenges to general compatibility of such two basic scientific disciplines as the thermodynamics and the quantum theory. In other words, either thermodynamics or quantum theory (or none of them) can apply as universal theories. Definitely not both of them.

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