Violation of the 2nd law of thermodynamics in the quantum microworld

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For one open quantum system recently reported to work as a perpetuum mobile of the second kind, basic equations providing basis for discussion of physics beyond the system activity are rederived in an appreciably simpler manner. The equations become exact in one specific scaling limit corresponding to the physical regime where internal processes (relaxations) in the system are commensurable or even slower than relaxation processes induced by bath. In the high-temperature (i.e. classical) limit, the system ceases to work, i.e., validity of the second law is reestablished.

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I Introduction

The quantum theory of open system [1–3] is perhaps the most important part of the nonequilibrium statistical physics, mainly owing to its impact on as complicated complex systems as living organisms. Mechanisms of energy, particle etc. transfer or transformation revealed by biologists are often connected with a particular feature of macromolecular systems - topological instability upon detecting presence of a particle, molecular group, excitation etc. on a specialized place called usually receptor [4]. In other words, complicated molecular systems adjust very fast to the presence of the species to be processed [4]. For, e.g., the particle transfer and in terms of the language of physics, this is nothing but a clear manifestation of so called dynamical correlations between, e.g., position of the particle and quantum statistical state of its surroundings. These dynamical correlations have been until recently only little investigated, in particular, in connection with their role in the particle transfer. Recently, one specific model of an open quantum system utilizing these correlations has been reported to violate the second law of thermodynamics [5–7]. The model, as again presented below, is complicated but possible simplifications [8] do not seem to amend the situation appreciably. That is why we shall stick,

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except for rather minor formal improvements, to its original form. We shall, however, present here another and much simpler form of derivation of basic equations. The method (equations of motion for quantum operators) is generally known from, e.g., the laser physics. It also becomes exact in one scaling limit. This may help in convincing general public that there is really no unjustified trick in the treatment.

This goal is of particular importance, because possible violation of one of basic laws of thermodynamics could appreciably change structure and mutual relations among scientific disciplines, as we understand them now. The reader should not be, however, surprised by the declared potential violation of one of the pillars of thermodynamics. Reports on such violations, in both theory and experiment, now become more and more numerous — see, e.g., [9–11] and papers cited therein. The first violation of the second law in experiment has been reported in 1995 [12] and has been so far not questioned. That is why one should feel sceptical but still open-minded in this rather contravening but rapidly developing part of theory.

The paper is organized as follows: In the next section, we describe the model and physical principles on which its activity is based. In Section 3, equations of motion are derived starting from the usual equations of motion for the Heisenberg operators. In Section 4, we discuss some special cases illustrating the reported behavior violating standard statistical mechanics. Reasons for this failure are to be looked for in specific correlations between particles and their surroundings. Standard statistical thermodynamics is based on an idea of a weak system-bath coupling what is insufficient for proper descriptions of such correlations.

II Model and description of its activity

The fully quantum Hamiltonian of our model in its simplest version can be as usual written as a sum of the Hamiltonians of the system, thermodynamic bath, and that of the system-bath interaction. Thus,

$$H = H_{\mathrm{S}} + H_{\mathrm{B}} + H_{S-B}, \tag{1}$$

where

$$\begin{aligned} H_{\mathrm{S}} = & \sum_{\iota=-\infty}^{+\infty} \{J(c^{\dagger}_{-1,\iota}c_{0,\iota} + c^{\dagger}_{0,\iota}c_{-1,\iota}) \cdot |d\rangle\langle d| + I(c^{\dagger}_{1,\iota}c_{0,\iota} + c^{\dagger}_{0,\iota}c_{1,\iota}) \cdot |u\rangle\langle u| \\ & + K(c^{\dagger}_{1,\iota}c_{-1,\iota+1} + c^{\dagger}_{-1,\iota+1}c_{1,\iota})\} + \frac{\Delta}{3} \sum_{m=-1}^{+1} \sum_{\iota=-\infty}^{+\infty} [3\iota + m] c^{\dagger}_{m,\iota}c_{m,\iota} \\ & + \frac{\epsilon}{2} \left[1 - 2 \sum_{\iota} c^{\dagger}_{0,\iota}c_{0,\iota} \right] [|u\rangle\langle u| - |d\rangle\langle d|] \end{aligned} \tag{2}$$

describes a particle that could be located at three sites ($m = -1$, 0, and 1) in a ring, and a two-level system with states $|d\rangle$ and $|u\rangle$ separated by energy gap ϵ. We assume $\epsilon > 0$. The particle is assumed to slide on a periodic (macro)molecule in form of a screw that cannot rotate but which is by the sliding molecule rotating

in the circle of sites '-1'↔'0'↔'$+1$' ↔ '-1' etc. forced to move up and down in a potential field. The molecular screw may be arbitrarily long; for formal reasons, we take it as infinite. Position on the thread to which the particle located at site m is connected is designated as m, ι. So, index m has a double meaning what should, however, cause no problems. Index ι then designates the turn of the thread to which the particle can be appended. There are several important features known from previous studies as well as Nature and incorporated in the Hamiltonian H_{S}:

- One can easily recognize that (2) is nothing but, up to small modification, the model of [5–7]. Here, however, the screw molecule is described already in H_{S}, i.e., it need not be additionally incorporated into theory as in the above papers. Clearly, $\Delta/3$ is the energy the macromolecular screw acquires, at the cost of the bath as shown below, upon one single particle hop '-1'→'0', '0'→'$+1$', or '$+1$'→'-1'. In connection with that, one should also understand the hopping integrals J, I, and K as not merely particle integrals but representing also inertial properties of the screw. This is why we can assume below that these integrals are sufficiently small.

- For $J = I = K = 0$ (practically, for small enough $|J|$, $|I|$ and $|K|$), the particle does not move and the central two-level system with states $|d\rangle$ and $|u\rangle$ can be analyzed separately, according to the position of the particle. What is important is the form of the particle vs. central system interaction which causes that the order of energy levels of the central system reverses once the particle is brought to site '0'. This is a kind of a topological instability known in Nature to appear when a specific type of particle appears at, e.g., molecular receptors.

- The resulting instability upon the particle leaving or arriving at site '0' has a far-reaching impact in connection with the transfer (hopping) terms $J(c^{\dagger}_{-1,\iota}c_{0,\iota} + c^{\dagger}_{0,\iota}c_{-1,\iota}) \cdot |d\rangle\langle d|$ and $I(c^{\dagger}_{1,\iota}c_{0,\iota} + c^{\dagger}_{0,\iota}c_{1,\iota}) \cdot |u\rangle\langle u|$. These particle transfer terms become effective just when the central two-level system is in states $|d\rangle$ and $|u\rangle$, respectively. One can assume, e.g., that transfer between two states of our central system might mean transfer of site '0' in space which may connect or disconnect molecular bridges between the particle sites. This mechanism ensures, upon dynamic and sufficiently fast transfers between states of the central system, effective blocking of the return channels of our particle. We know this behavior from molecular pumps.

Worth noticing is that in (2), the forth and back transfers in any pair of the sites are always with the same amplitude as a consequence of the hermicity of H_{S}. The one-directional character of the process reported here is not owing to a contingent difference between these amplitudes but results exclusively (as it will become clear later on) from the existence of spontaneous processes between states $|u\rangle$ and $|d\rangle$ of the central system. The reason is that these are the spontaneous processes that cause different population of central-system states $|u\rangle$ and $|d\rangle$, i.e., cause effective blocking of the back particle-transfer channels. Dynamic transitions between states

of our central system according to the instantaneous position of the particle is the basis of what is known about, e.g., activity connected with topological changes of real biomolecules working as molecular machines [4].

As for the Hamiltonians of the bath H_{B}, we assume the standard form of non-interacting bosons (phonons)

$$H_{\mathrm{B}} = \sum_k \hbar\omega_k b_k^\dagger b_k \,, \tag{3}$$

where b_k and $b_k^\dagger$ fulfil standard Bose commutational relations and ω_k represents the boson frequency. Finally, one should specify Hamiltonian of the system-bath coupling $H_{\mathrm{S-B}}$. First of all, we must keep in mind that there are two roles played by $H_{\mathrm{S-B}}$. This is the particle dephasing among different sites what conditions breaking of covalent bonds among the sites necessary for the particle flow. Second, we need that $H_{\mathrm{S-B}}$ causes transitions between states $|u\rangle$ and $|d\rangle$ of our central system. These transfers ensure the dynamic blocking of the particle hopping integrals mentioned above what forms, in connection with uncertainty relations making localization of particle at one site energetically disadvantageous, the real reason why the particle starts to move in the direction that is allowed. This is the reason for appearance of the stationary flow utilized below. Such transfers between states $|u\rangle$ and $|d\rangle$ of our central system could also cause particle dephasing, i.e. breaking of the particle covalent bonds. Such a dephasing would become effective just in higher orders of the perturbation theory (see below). That is why we assume $H_{\mathrm{S-B}}$ to consist of two terms which separately give rise to the $|u\rangle \leftrightarrow |d\rangle$ transitions and the on-site dephasing. So, we take

$$H_{\mathrm{S-B}} = \frac{1}{\sqrt{N}} \sum_k \hbar\omega_k (b_k + b_{-k}^\dagger) \left\{ G_k [|u\rangle\langle d| + |d\rangle\langle u|] + \sum_{m=-1}^{+1} \sum_{\iota=-\infty}^{+\infty} g_k^m c_{m,\iota}^\dagger c_{m,\iota} \right\}$$

$$\equiv H'_{\mathrm{S-B}} + H''_{\mathrm{S-B}}. \tag{4}$$

For the sake of technical simplicity, we assume that $H'_{\mathrm{S-B}}$ and $H''_{\mathrm{S-B}}$ do not interfere. This may be ensured by assuming that condition $g_k G_k^* = 0$ applies for each k. This condition, however, does not imply existence of two different baths.

One comment is still worth mentioning here before we come to technical problems below. We intend to prove that the mechanism encoded in the above model may provide a perpetuum mobile of the second kind. There are, however, intuitive arguments against such a possibility saying that one cannot in general control phase (i.e. proper time of arrival) of excitations from the bath to be able to utilize their energy in a prescribed manner and at a proper time. This utilization should take place, for a macroscopic energy effect, using a constructive superposition of the elementary acts of the bath excitation (phonon) absorption. This constructive superposition should efficiently suppress processes of the phonon (excitation) emission which, unfortunately, (as particle downhill processes) prevail once the system in question has been previously excited by absorbing a previously arriving excitation. The latter feature is what is commonly believed to hinder macroscopic energy

gains at the cost of just thermal energy from the bath. Here, however, our system *is* able to act in the prescribed manner. Really, as already argued above (and as it will be used below), the hopping terms are to be assumed to be the smallest ones in the total Hamiltonian (or at most commensurable with transfer rates between two states of our central system). This means a very slow particle transfer. Assume, e.g., that the particle hopped from site '-1' to site '0'. As seen from (2), 'site + central-system' energy increased in such a case by the amount $\epsilon+\Delta/3$. This amount cannot be, however, so far considered as a real energy gain as the transfer was elastic and site off-diagonal density matrix elements $\rho_{-1,\iota,\ldots;0,\iota',\ldots}$ still remain nonzero (there is still a covalent bonding between sites '-1' and '0'). Now, the second stage of the transfer comes, where, because of the Hamiltonian $H''_{\mathrm{S-B}}$, fast dephasing suppresses density matrix elements $\rho_{-1,\iota,\ldots;0,\iota',\ldots}$. Only then one can consider $\epsilon+\Delta/3$ as an energy gain. What is its source? This is the thermal bath, as dephasing is nothing but a continuous absorption and emission of phonons (compare the form of $H''_{\mathrm{S-B}}$ in (4)). Simultaneously, however, the system loses energy ϵ because the central system reconstructs, transferring (at low temperatures) from state $|d\rangle$ to state $|u\rangle$. This energy is returned to the bath so that the net energy gain is $\Delta/3$. This is in fact the gain we work with. Now, because of transfer of the central system to state $|u\rangle$, the particle has already blocked the return channel; it cannot get back to site '-1' (returning thus, after next dephasing, the energy portion $\Delta/3$ to the bath again) and can only continue to the next site '$+1$'. Classical particle would not do that but quantum particles cannot (for reasons connected with uncertainty relations) remain localized at any single site. At site '$+1$', however, the story is repeated and finally, upon the whole turn of the particle, the system 'particle + the molecular screw' acquires energy Δ, fully at the cost of the thermal bath during the dephasing process. The latter process is ineffective from the point of view of the particle energy at general times. It becomes, however, in the manner described above, highly effective immediately after the particle transfer. That provides the proper timing necessary for utilization of the energy of the thermal excitations from the bath which thus appears possible irrespective of the fact that the excitations are mutually fully out-of-phase. The reader should convince himself/herself that the energy gain is thus, fully surprisingly, caused by a specific combination of delocalization behavior of quantum particles, dephasing, and prevailing down-hill (in energy) transfers due to spontaneous processes inside the (central part of the) system. All these phenomena are purely quantum ones. That is also why no classical analogue of the present model can work.

A bit more arguments are perhaps needed in connection with the above statement that the particle cannot return from site '0' (with the two-level system relaxed to state $|u\rangle$) back to site '-1' (with ensuing relaxation of the two-level system back to state $|d\rangle$). In fact, such processes can really appear and could be of two possible types:

- As a higher-order process where, between the asymptotic (initial and final) states, the two-level system must be first excited to state $|d\rangle$ (to open the transfer channel for the particle) and then the particle is transferred, by the

first term on the right hand side of (2) (that is $\propto J$), back to site '-1'. (In other words, the excitation of the two-level system $|u\rangle \rightarrow |d\rangle$ is just a virtual process.) This requires, however, a higher-order perturbational contribution (second-order in the amplitudes, i.e. fourth-order for the probabilities or in coefficients of the kinetic equations for diagonal as well as off-diagonal elements of the density matrix). Such terms become thus negligible in the scaling limit used here (and corresponding to the regime investigated) in which only second-order terms survive — see below or [13]. Physically, such higher-order terms become negligible owing to presumed smallness of the transfer terms (as compared to the reciprocal time unit used).

- Second possibility for the above combined back-transfer '0'→'-1' is that it is a consequence of two independent real (i.e. not virtual) processes. Such a possibility is in fact properly included into our formalism, and is connected with terms $\propto \Gamma_\uparrow$ [1]) determining, *inter alia*, the probability (per second) of excitation $|u\rangle \rightarrow |d\rangle$ with the particle still residing at site '0'. The fact that (for $k_\mathrm{B}T \ll \epsilon$) $\Gamma_\uparrow = \Gamma_\downarrow \exp(-\epsilon/(k_\mathrm{B}T)) \ll \Gamma_\downarrow$ explains why these processes result as less effective and why the particle prevailingly choses, upon arriving at site '0' and after the ensuing relaxation of the two-level system to state $|u\rangle$, going rather to site '$+1$'. For such a process, there is (for $\Delta \ll \epsilon$) no similar suppressing statistical factor able to compete $\exp(-\epsilon/(k_\mathrm{B}T)) \ll 1$ above. On the other hand, for $k_\mathrm{B}T \gtrsim \epsilon$, $\Gamma_\uparrow$ becomes comparable with $\Gamma_\downarrow$. That is why our approach below really yields why the net effect disappears at high enough temperatures.

With that, let us now have a look at dynamic equations to which the chosen model (working as described above) leads.

III Equations of motion

Technically, in our theory here, we shall *not* follow [5–7]. The reason is not connected with a tiny difference in the Hamiltonian but is, rather, due to little acquaintance of general public with the projection method of Tokuyama and Mori [14] used in [5–7]. Instead, we use here a method that belongs to a standard weaponry of theoretical physics — equation of motion method. Before its application, one should add a few words considering small parameters of the problem and, thus, arguments in favor of omission of terms that are of minor importance and, consequently, disappear in a properly performed scaling limit.

Above, we have already mentioned that hopping (transfer or resonance) integrals J, I, and K are, for deeply physical reasons, rather small. We shall be interested in the regime where their respective time scales, i.e. $\hbar/|J|$ etc., are longer than (or at least commensurable with) those corresponding to the relevant bath-assisted processes. There are two such type of processes: The first type processes are those

[1]) See (5) below for definitions of transfer rates $\Gamma_\uparrow$ and $\Gamma\downarrow$ which are nothing but Golden Rule transfer rates for transitions between two levels of our two-level system.

describing mutual transitions (re-relaxation) between states $|u\rangle$ and $|d\rangle$. The corresponding up-hill and down-hill transfer rates read (up to higher-order corrections that become irrelevant upon proper scaling)

$$\begin{aligned} \Gamma_{\downarrow} &= \frac{2\pi}{N\hbar}\sum_k (\hbar\omega_k)^2 |G_k|^2 [1+n_{\rm B}(\hbar\omega_k)]\delta(\hbar\omega_k-\epsilon), \\ \Gamma_{\uparrow} &= \frac{2\pi}{N\hbar}\sum_k (\hbar\omega_k)^2 |G_k|^2 n_{\rm B}(\hbar\omega_k)\delta(\hbar\omega_k-\epsilon) = \exp(-\beta\hbar\omega_k)\Gamma_{\downarrow}. \end{aligned} \tag{5}$$

Here $n_{\rm B}(z) = [\exp(\beta z)-1]^{-1}$ is the Bose–Einstein–Planck distribution for phonons and $\beta = 1/(k_{\rm B}T)$ is the reciprocal (initial) temperature of our phonon bath in energy units. Clearly, $\Gamma_{\downarrow}$ and $\Gamma_{\uparrow}$ are the second-order Golden rule transfer rates between the above states of the central system caused by $H'_{\rm S-B}$ in (4). So, the first necessary requirement for the regime we are interested in is that

$$\frac{|J|}{\hbar},\ \frac{|I|}{\hbar} \ll 0.5(\Gamma_{\uparrow}+\Gamma_{\downarrow}). \tag{6}$$

The second necessary condition is connected with the third transfer integral K describing particle transitions directly between sites $+1$ and -1. We require that

$$\frac{|K|}{\hbar} \ll 2\Gamma_{-1,1}. \tag{7}$$

Here

$$2\Gamma_{mn} = \frac{\pi}{N\hbar}\sum_k (\hbar\omega_k)^2 |g_k^m - g_k^n|^2 [1+2n_{\rm B}(\hbar\omega_k)]\delta_{\gamma}(\hbar\omega_k), \tag{8}$$

where $\delta_{\gamma}(x)$ designates the δ-function properly (selfconsistently, as a Lorentzian) broadened by all the dephasing processes on the sites involved [2]) So, 2Γ is the dephasing rate caused by the second term in (4), i.e. by $H''_{\rm S-B}$. Conditions (6–7) could be a bit relaxed by replacing sign $\ll$ by $\lesssim$ but it would not change physics of our problem. In any case, ratio of the right and left hand sides in (6–7) should be kept finite.

These conditions imply that the physical regime we are interested in is certainly not that one of the weak coupling to the bath. So we must refrain from the weak coupling theory. In accordance with [7] (see also [13] for mathematical details), we introduce a formal parameter λ and set

$$I,\ J,\ K \propto \lambda^2, \quad H_{\rm S-B} \propto \lambda. \tag{9}$$

Next, in the equations of motion below, we shall only keep all terms upto the order λ^2 and use mathematics (originally due to Davies [15, 16]) ensuring that after introducing a new time-unit $\propto \lambda^{-2}$, all terms of higher (than second) order in λ disappear. Readers more interested in details of this scaling are referred to [13].

[2]) Those who could feel embarrassed by necessity to incorporate the broadening, could, e.g., replace $H''_{\rm S-B}$ in (4) by another form incorporating two-phonon processes. This leads, however, to no qualitative change.

This is the spirit of the method. Now let us have a look how it works in practice. First of all, we transfer all the operators into the Heisenberg picture, using the prescription

$$A(t) \equiv \mathrm{e}^{\mathrm{i}H\cdot t/\hbar} A \mathrm{e}^{-\mathrm{i}H\cdot t/\hbar} \tag{10}$$

This implies that

$$\frac{\mathrm{d}}{\mathrm{d}t}A(t) = \frac{\mathrm{i}}{\hbar}[H, A](t). \tag{11}$$

The commutators on the right hand side of (11) have to be evaluated. So, for instance,

$$\frac{\mathrm{d}}{\mathrm{d}t}b_k(t) = \frac{\mathrm{i}}{\hbar}[H, b_k](t) = -\mathrm{i}\omega_k b_k(t) - \frac{\mathrm{i}}{\sqrt{N}}\left\{G_k^*\sigma_x(t) + \sum_{m=-1}^{+1}(g_k^m)^* \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(t)\right\},$$

$$\frac{\mathrm{d}}{\mathrm{d}t}b_k^\dagger(t) = \mathrm{i}\omega_k b_k^\dagger(t) + \frac{\mathrm{i}}{\sqrt{N}}\left\{G_k\sigma_x(t) + \sum_{m=-1}^{+1}(g_k^m) \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(t)\right\}, \tag{12}$$

$$\sigma_x = |u\rangle\langle d| + |d\rangle\langle u|, \sigma_y = -\mathrm{i}[|u\rangle\langle d| - |d\rangle\langle u|], \sigma_z = |u\rangle\langle u| - |d\rangle\langle d|.$$

The solution reads

$$b_k(t) = \mathrm{e}^{-\mathrm{i}\omega_k t}b_k(0) - \frac{\mathrm{i}\omega_k}{\sqrt{N}}\int_0^t \left\{G_k^*\sigma_x(\tau) + \sum_{m=1}^{+1}(g_k^m)^* \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(\tau)\right\} \mathrm{e}^{-\mathrm{i}\omega_k(t-\tau)}\,\mathrm{d}\tau,$$

$$b_k^\dagger(t) = \mathrm{e}^{\mathrm{i}\omega_k t}b_k^\dagger(0) + \frac{\mathrm{i}\omega_k}{\sqrt{N}}\int_0^t \{G_k\sigma_x(\tau) + \sum_{m=1}^{+1} g_k^m \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(\tau)\}\mathrm{e}^{\mathrm{i}\omega_k(t-\tau)}\,\mathrm{d}\tau. \tag{13}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|](t) = \frac{\mathrm{i}}{\hbar}[H, c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|](t). \tag{14}$$

Evaluating the commutator and putting here (13), we get

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}[c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|](t) &= \frac{\mathrm{i}\Delta}{3\hbar}[c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|](t) + \frac{\mathrm{i}}{\hbar}J((c_{0,\iota}^\dagger c_{0,\iota} - c_{-1,\iota}^\dagger c_{-1,\iota}) \\
&\otimes |d\rangle\langle d|)(t) + \frac{\mathrm{i}}{\hbar}K(c_{1,\iota-1}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t) - \frac{\mathrm{i}}{\hbar}\epsilon(c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t) + F_{-\,d,0\,d}^{\iota} \\
&+ \frac{\mathrm{i}}{N}\sum_k \omega_k^2 G_k \int_0^t (-2\sin(\omega_k(t-\tau)) \\
&\times \left[\left\{G_{-k}\sigma_x(\tau) + \sum_{m=-1}^{+1} g_{-k}^m \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(\tau)\right\}(c_{-1,\iota}^\dagger c_{0,\iota} \otimes |u\rangle\langle d|)(t)\right. \\
&\left. - (c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle u|)(t)\left\{G_{-k}\sigma_x(\tau) + \sum_{m=-1}^{+1} g_{-k}^m \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(\tau)\right\}\right]\mathrm{d}\tau \\
&+ \frac{\mathrm{i}}{N}\sum_k \omega_k^2 \int_0^t (-2\sin(\omega_k(t-\tau)) \times
\end{aligned}$$

$$\times \left[g_k^{-1} \left\{ G_{-k}\sigma_x(\tau) + \sum_{m=-1}^{+1} g_{-k}^m \sum_\iota (c_{m,\iota}^\dagger c_{m,\iota})(\tau) \right\} (c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t) \right.$$
$$\left. - g_k^0 \sum_\iota (c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t) \left\{ G_{-k}\sigma_x(\tau) + \sum_{m=-1}^{+1} \sum_\iota g_{-k}^m (c_{m,\iota}^\dagger c_{m,\iota})(\tau) \right\} \right] \mathrm{d}\tau. \quad (15)$$

Here

$$\begin{aligned} F_{-\,d,0\,d}^{\iota} = & \frac{\mathrm{i}}{\sqrt{N}} \sum_k \omega_k G_k [(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b_{-k}(0)^\dagger \mathrm{e}^{\mathrm{i}\omega_k t})(c_{-1,\iota}^\dagger c_{0,\iota} \otimes |u\rangle\langle d|)(t) \\ & - (c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle u|)(t)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b_{-k}(0)^\dagger \mathrm{e}^{\mathrm{i}\omega_k t})] \\ & + \frac{\mathrm{i}}{\sqrt{N}} \sum_k \omega_k [g_k^{-1}(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b_{-k}(0)^\dagger \mathrm{e}^{\mathrm{i}\omega_k t})(c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t) \\ & - g_k^0 (c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b_{-k}(0)^\dagger \mathrm{e}^{\mathrm{i}\omega_k t})]. \end{aligned} \quad (16)$$

Now, one should realize that also the transfer (hopping or resonance) integrals J, I, and K are scaled as $\propto \lambda^2$ in our approach. Because the last two terms on the right hand side of (15) are already of the second order in the small scaling parameter λ, we can work to just the zeroth order, i.e., we can omit, for purposes of evaluation of the last two terms in (15), the hopping integrals completely. This yields

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\sigma_x(t) = & \frac{\mathrm{i}}{\hbar}[H,\sigma_x](t) \approx \\ & \frac{\mathrm{i}}{\hbar}\frac{\epsilon}{2}\left[\left(1 - 2\sum_\iota c_{0,\iota}^\dagger c_{0,\iota} \right) \sigma_z, \sigma_x \right](t) = -\frac{\epsilon}{\hbar} \left(1 - 2\sum_\iota c_{0,\iota}^\dagger c_{0,\iota} \right) \sigma_y(t), \\ \frac{\mathrm{d}}{\mathrm{d}t}\sigma_y(t) = & \frac{\mathrm{i}}{\hbar}[H,\sigma_y](t) \approx \\ & \frac{\mathrm{i}}{\hbar}\frac{\epsilon}{2}\left[\left(1 - 2\sum_\iota c_{0,\iota}^\dagger c_{0,\iota} \right) \sigma_z, \sigma_y \right](t) = \frac{\epsilon}{\hbar} \left(1 - 2\sum_\iota c_{0,\iota}^\dagger c_{0,\iota} \right) \sigma_x(t). \end{aligned} \quad (17)$$

Here, in the given order, $c_{0,\iota}^\dagger c_{0,\iota}$ can be already considered as time-independent, i.e. at the initial time $t = 0$. From (17), we get

$$\begin{aligned} \sigma_x(\tau) &\approx \sigma_x(t)\cos\left[\frac{\epsilon}{\hbar}(\tau - t)\right] - \left(1 - 2\textstyle\sum_\iota c_{0,\iota}^\dagger c_{0,\iota}\right)\sigma_y(t)\sin\left[\frac{\epsilon}{\hbar}(\tau - t)\right], \\ \sigma_y(\tau) &\approx \left(1 - 2\textstyle\sum_\iota c_{0,\iota}^\dagger c_{0,\iota}\right)\sigma_x(t)\sin\left[\frac{\epsilon}{\hbar}(\tau - t)\right] + \sigma_y(t)\cos\left[\frac{\epsilon}{\hbar}(\tau - t)\right]. \end{aligned} \quad (18)$$

Next, we shall use the assumption of non-interference of dephasing and transitions $g_k^m G_k = 0$. This yields

$$\frac{\mathrm{d}}{\mathrm{d}t}[c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|](t) \approx \frac{\mathrm{i}}{\hbar} J((c_{0,\iota}^\dagger c_{0,\iota} - c_{-1,\iota}^\dagger c_{-1,\iota}) \otimes |d\rangle\langle d|)(t) +$$

$$+\frac{\mathrm{i}}{\hbar}K(c^{\dagger}_{1,\iota-1}c_{0,\iota}\otimes|d\rangle\langle d|)(t)-\frac{\mathrm{i}}{\hbar}\epsilon(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(t)+F^{\iota}_{-\,d,0\,d}$$

$$+\frac{\mathrm{i}}{N}\sum_k\omega_k^2\int_0^t(-2\sin(\omega_k(t-\tau)))[|g_k^{-1}|^2-|g_k^0|^2]\,\mathrm{d}\tau(c^{\dagger}_{-1,\iota}c_{\iota}0\otimes|d\rangle\langle d|)(t). \quad (19)$$

Here, we have neglected $\Delta/3$ as compared to ϵ what amounts to neglecting a weak Δ-dependence of transfer rates.

Now, we must evaluate $F^{\iota}_{-\,d,0\,d}$ in detail. For this purpose, to the first order in λ and again neglecting $\Delta/3$ as compared to ϵ, we get using again the equations of motion for the corresponding operators that

$$\begin{aligned}
&(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(t)\approx \mathrm{e}^{-\mathrm{i}\epsilon t/\hbar}(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(0)\\
&\quad+\frac{\mathrm{i}}{\sqrt{N}}\sum_k\omega_k\int_0^t\{g_k^{-1}(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau})(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)\\
&\quad-g_k^0(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau})\}\,\mathrm{d}\tau,\\
&(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle u|)(t)\approx(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle u|)(0)\\
&\quad+\frac{\mathrm{i}}{\sqrt{N}}\sum_k\omega_k\int_0^t G_k\{(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau})(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|u\rangle\langle u|)(\tau) \quad (20)\\
&\quad-(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau}\}\,\mathrm{d}\tau,\\
&(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|u\rangle\langle d|)(t)\approx(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|u\rangle\langle d|)(0)\\
&\quad+\frac{\mathrm{i}}{\sqrt{N}}\sum_k\omega_k\int_0^t G_k\{(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau})(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)\\
&\quad-(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|u\rangle\langle u|)(\tau)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k\tau}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k\tau}\}\,\mathrm{d}\tau.
\end{aligned}$$

Now we use (21) in (16) and put everything into (15). We get

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}[c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|](t)\approx\frac{\mathrm{i}}{\hbar}J((c^{\dagger}_{0,\iota}c_{0,\iota}-c^{\dagger}_{-1,\iota}c_{-1,\iota})\otimes|d\rangle\langle d|)(t)\\
&+\frac{\mathrm{i}}{\hbar}K(c^{\dagger}_{1,\iota-1}c_{0,\iota}\otimes|d\rangle\langle d|)(t)+\frac{\mathrm{i}}{\hbar}\left(\frac{\Delta}{3}-\epsilon\right)(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(t)+I^{\iota}_{-1\,d,0\,d}(t)\\
&+\frac{\mathrm{i}}{N}\sum_k\omega_k^2\int_0^t(-2\sin(\omega_k\tau))[|g_k^{-1}|^2-|g_k^0|^2](c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(t)\mathrm{d}\tau\\
&-\frac{1}{N}\sum_{k,k'}\omega_k g_k^{-1}(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t}+b^{\dagger}_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})\int_0^t\mathrm{e}^{-\mathrm{i}\epsilon(t-\tau)/\hbar}\omega_{k'}\\
&\times\{g_{k'}^{-1}(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau}+b^{\dagger}_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)\\
&-g^0_{k'}(c^{\dagger}_{-1,\iota}c_{0,\iota}\otimes|d\rangle\langle d|)(\tau)(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau}+b^{\dagger}_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})\}\,\mathrm{d}\tau\\
&+\frac{1}{N}\sum_{k,k'}\omega_k g_k^0\int_0^t\mathrm{e}^{-\mathrm{i}\epsilon(t-\tau)/\hbar}\omega_{k'}\{g_{k'}^{-1}(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau}+b^{\dagger}_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})\times
\end{aligned}$$

$$\times (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(\tau) - g^0_{k'}(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(\tau)$$
$$\times (b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau} + b^\dagger_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})\}\,\mathrm{d}\tau\,(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})$$
$$-\frac{1}{N}\sum_{k,k'} G_k(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t}+b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})\int_0^t G_{k'}\{(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau}+b^\dagger_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})$$
$$\times (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(\tau) - (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle u|)(\tau)(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau} + b^\dagger_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})\}\,\mathrm{d}\tau$$
$$+\frac{1}{N}\sum_{k,k'} G_k\int_0^t G_{k'}\{(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau} + b^\dagger_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle u|)(\tau)$$
$$- (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(\tau)(b_{k'}(0)\mathrm{e}^{-\mathrm{i}\omega_{k'}\tau} + b^\dagger_{-k'}(0)\mathrm{e}^{\mathrm{i}\omega_{k'}\tau})\}\,\mathrm{d}\tau$$
$$\times (b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t}). \tag{21}$$

Here

$$I^\iota_{-1\,d,0\,d}(t) = \frac{\mathrm{i}}{\sqrt{N}}\sum_k \omega_k G_k\{(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle d|)(0)$$
$$- (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle u|)(0)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})\}$$
$$+\frac{\mathrm{i}}{\sqrt{N}}\sum_k \omega_k\{g_k^{-1}(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(0)$$
$$- g^0_k(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(0)(b_k(0)\mathrm{e}^{-\mathrm{i}\omega_k t} + b^\dagger_{-k}(0)\mathrm{e}^{\mathrm{i}\omega_k t})\}\mathrm{e}^{-\mathrm{i}\epsilon t/\hbar} \tag{22}$$

is a stochastic force. Now we shall preserve just terms with creation and annihilation operators of phonons with $k' = -k$ (other terms disappear upon taking average with the initial density matrix of the bath in the canonical form) and use that, within the lowest order in λ, $(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(\tau) \approx (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(t)\exp(\mathrm{i}\epsilon(t-\tau)/\hbar)$ and similarly $(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle u|)(\tau) \approx (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle u|)(t)\exp(-\mathrm{i}\epsilon(t-\tau)/\hbar)$. Also the use may be made of the fact that within the relaxation terms and within the required second order, creation and annihilation operators of the particle, those of the bath, and of the two-level system may be taken as commuting (commutators yield higher-order terms). Then, after some algebra and identification $\int_0^t \exp(\pm\mathrm{i}\omega\tau)\,\mathrm{d}\tau \approx_{t\to+\infty} \pi\delta(\omega)$ [3]) (21) reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}[c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|](t) \approx \frac{\mathrm{i}}{\hbar}J((c^\dagger_{0,\iota}c_{0,\iota} - c^\dagger_{-1,\iota}c_{-1,\iota}) \otimes |d\rangle\langle d|)(t)$$
$$+\frac{\mathrm{i}}{\hbar}K(c^\dagger_{1,\iota-1}c_{0,\iota} \otimes |d\rangle\langle d|)(t) + \frac{\mathrm{i}}{\hbar}\left(\frac{\Delta}{3} - \epsilon\right)(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(t) + I^\iota_{-1\,d,0\,d}(t)$$
$$+\frac{1}{2}\frac{2\pi}{\hbar}\frac{1}{N}\sum_k(\hbar\omega_k)^2|G_k|^2\delta(\epsilon - \hbar\omega_k)[1 + 2b^\dagger_k(0)b_k(0)]\{(c^\dagger_{-1,\iota}c_{0,\iota} \otimes |u\rangle\langle u|)(t)$$
$$- (c^\dagger_{-1,\iota}c_{0,\iota} \otimes |d\rangle\langle d|)(t)\} - \frac{1}{2}\frac{2\pi}{\hbar}(\hbar\omega_k)^2|g_k^{-1} - g^0_k|^2\delta_\gamma(\hbar\omega_k) \times$$

[3]) As usual, error caused by this step can be reduced to a renormalization of terms already present.

$$\times [1 + 2b_k^\dagger(0)b_k(0)](c_{-1,\iota}^\dagger c_{0,\iota} \otimes |d\rangle\langle d|)(t). \tag{23}$$

Here $\delta_\gamma(...)$ is to be understood as a δ-function broadened by transversal relaxation processes. We then identify

$$2\Gamma = \frac{1}{2}\frac{2\pi}{\hbar}(\hbar\omega_k)^2|g_k^{-1} - g_k^0|^2\delta_\gamma(\hbar\omega_k)[1 + 2b_k^\dagger(0)b_k(0)], \tag{24}$$

$$\Gamma_\downarrow = \frac{2\pi}{\hbar}\frac{1}{N}\sum_k(\hbar\omega_k)^2|G_k|^2\delta(\epsilon - \hbar\omega_k)[1 + b_k^\dagger(0)b_k(0)], \tag{25}$$

and

$$\Gamma_\uparrow = \frac{2\pi}{\hbar}\frac{1}{N}\sum_k(\hbar\omega_k)^2|G_k|^2\delta(\epsilon - \hbar\omega_k)b_k^\dagger(0)b_k(0). \tag{26}$$

(Clearly, (24–26) are nothing but (5) and (8) in the operator form.) Then (23) is the final operator equation that we aim at here. We now multiply it by the initial density matrix $\rho(0)$ of the system and the bath (which are initially assumed uncorrelated), assume the initial density matrix of the bath to be canonical, and take the trace. Finally, we define the density matrix of the reduced system, i.e. of the particle and the two-level central system, as

$$\rho_{m\alpha,n\gamma}(t) = \sum_\iota \mathrm{Tr}(\rho(0)(c_{n,\iota}^\dagger c_{m,\iota})(t) \otimes (|\gamma\rangle\langle\alpha|)(t)),$$

$$|\alpha\rangle \text{ and } |\gamma\rangle \text{ being } |u\rangle \text{ or } |d\rangle. \tag{27}$$

Presuming then that dependence on ι, ι' of $\mathrm{Tr}(\rho(0)(c_{n,\iota}^\dagger c_{m,\iota'})(t) \otimes (|\gamma\rangle\langle\alpha|)(t))$ is smooth, and summing up the result over ι, we immediately obtain the fifteenth equation of the set (14) of [7]. Let us only add that the above smooth dependence on ι, ι' is a result of very small dephasing processes applied to the state of the molecular screw.

In a fully analogous way, one can rederive all the remaining equations. In order to write them down explicitly here, we arrange all the 36 matrix elements $\rho_{\alpha\gamma}(t)$ in groups of nine designating

$$(\rho_{uu})^{\mathrm{T}} = \Big(\rho_{-1u,-1u}, \rho_{0u,0u}, \rho_{1u,1u}, \rho_{-1u,0u}, \rho_{-1u,1u}, \rho_{0u,-1u}, \rho_{0u,1u}, \rho_{1u,-1u}, \rho_{1u,0u}\Big),$$
$$(\rho_{dd})^{\mathrm{T}} = \Big(\rho_{-1d,-1d}, \rho_{0d,0d}, \rho_{1d,1d}, \rho_{-1d,0d}, \rho_{-1d,1d}, \rho_{0d,-1d}, \rho_{0d,1d}, \rho_{1d,-1d}, \rho_{1d,0d}\Big),$$
$$(\rho_{ud})^{T} = \Big(\rho_{-1u,-1d}, \rho_{0u,0d}, \rho_{1u,1d}, \rho_{-1u,0d}, \rho_{-1u,1d}, \rho_{0u,-1d}, \rho_{0u,1d}, \rho_{1u,-1d}, \rho_{1u,0d}\Big) \tag{28}$$

and similarly for ρ_{du}. Superscript $\cdots^{\mathrm{T}}$ designates transposition. With all that and proceeding in all technical details analogously as above, we obtain the set

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\rho_{uu}\\ \rho_{dd}\\ \rho_{ud}\\ \rho_{du}\end{pmatrix} = \begin{pmatrix}\mathcal{A}\,\mathcal{B} & \mathbf{0} & \mathbf{0}\\ \mathcal{C}\,\mathcal{D} & \mathbf{0} & \mathbf{0}\\ \mathbf{0}\,\mathbf{0}\cdots\cdots & & \\ \mathbf{0}\,\mathbf{0}\cdots\cdots & & \end{pmatrix}\cdot\begin{pmatrix}\rho_{uu}\\ \rho_{dd}\\ \rho_{ud}\\ \rho_{du}\end{pmatrix}. \tag{29}$$

Here, in the square matrix, all the elements are in fact blocks 9×9. Hence, the whole set splits into two independent sets of 18 equations each. That is why we shall be interested here in just that one for ρ_{uu} and ρ_{dd}. This reads as in (29) with typical forms of the block 9×9 matrices $\mathcal{A},\mathcal{B},\mathcal{C}$ and $\mathcal{D}$. In order to make the presentation as simple as possible, we first fully neglect the above Hamiltonian $H''_{\mathrm{S-B}}$ describing a direct coupling of the particle to the bath, responsible for the above additional dephasing. A direct calculation then yields

$$\mathcal{A} = \begin{pmatrix}
-\Gamma_\downarrow & 0 & 0 & 0 & \mathrm{i}\hbar & 0 & 0 & -\mathrm{i}K/\hbar & 0\\
0 & -\Gamma_\uparrow & 0 & 0 & 0 & 0 & \mathrm{i}I/\hbar & 0 & -\mathrm{i}I/\hbar\\
0 & 0 & -\Gamma_\downarrow & 0 & -\mathrm{i}K/\hbar & 0 & -\mathrm{i}I/\hbar & \mathrm{i}K/\hbar & \mathrm{i}I/\hbar\\
0 & 0 & 0 & k+\frac{\mathrm{i}\Delta}{3\hbar} & \mathrm{i}I/\hbar & 0 & 0 & 0 & -\mathrm{i}K/\hbar\\
\mathrm{i}K/\hbar & 0 & -\mathrm{i}K/\hbar & \mathrm{i}I/\hbar & -\Gamma_\downarrow-\frac{\mathrm{i}\Delta}{3\hbar} & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & k^*-\frac{\mathrm{i}\Delta}{3\hbar} & \mathrm{i}K/\hbar & -\mathrm{i}I/\hbar & 0\\
0 & \mathrm{i}I/\hbar & -\mathrm{i}I/\hbar & 0 & 0 & \mathrm{i}K/\hbar & k^*+\frac{\mathrm{i}\Delta}{3\hbar} & 0 & 0\\
-\mathrm{i}K/\hbar & 0 & \mathrm{i}K/\hbar & 0 & 0 & -\mathrm{i}I/\hbar & 0 & -\Gamma_\downarrow+\frac{\mathrm{i}\Delta}{3\hbar} & 0\\
0 & -\mathrm{i}I/\hbar & \mathrm{i}I/\hbar & -\mathrm{i}K/\hbar & 0 & 0 & 0 & 0 & k-\frac{\mathrm{i}\Delta}{3\hbar}
\end{pmatrix}. \tag{30}$$

Here $k = -\mathrm{i}\epsilon/\hbar - 0.5(\Gamma_\uparrow + \Gamma_\downarrow)$ with all the rates defined already by (5) and (8), and $\cdots^*$ designates complex conjugation. Let us mention that via $\Gamma_\uparrow$ and $\Gamma_\downarrow$, the initial bath temperature T (entering the problem via the initial bath density matrix ρ_{B}) enters the game. The rates $\Gamma_\uparrow$ and $\Gamma_\downarrow$ are known from the usual Pauli Master Equation approach to general kinetic problems. Still, however, our theory is (via inclusion of also the off-diagonal elements of ρ) much more rigorous including many higher-order processes. One can check that by formally excluding the off-diagonal elements of ρ from (29). For the diagonal ones, one then gets a set of time-convolution equations with kernels (memories) partially summed up to the infinite order. The resulting decay of the memories (owing to nonzero values of $\Gamma_\uparrow$ and $\Gamma_\downarrow$) then implies the required broadening of the original lowest-order energy conservation law, allowing transitions that were forbidden in the lowest order by the lowest-order energy arguments.

As for the block $\mathcal{B}$, it is fully diagonal with diagonal elements $\mathcal{B}_{11},\ldots,\mathcal{B}_{99}$ equal to $\Gamma_\uparrow$, $\Gamma_\downarrow$, $\Gamma_\uparrow$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $\Gamma_\uparrow$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, $\Gamma_\uparrow$ and $(\Gamma_\uparrow+\Gamma_\downarrow)/2$, respectively. Next,

$$\mathcal{D}=\begin{pmatrix}
-\Gamma_\uparrow & 0 & 0 & \mathrm{i}J/\hbar & \mathrm{i}K/\hbar & -\mathrm{i}J/\hbar & 0 & -\mathrm{i}K/\hbar & 0\\
0 & -\Gamma_\downarrow & 0 & -\mathrm{i}J/\hbar & 0 & \mathrm{i}J/\hbar & 0 & 0 & 0\\
0 & 0 & -\Gamma_\uparrow & 0 & -\mathrm{i}K/\hbar & 0 & 0 & \mathrm{i}K/\hbar & 0\\
\mathrm{i}J/\hbar & -\mathrm{i}J/\hbar & 0 & k^*+\dfrac{\mathrm{i}\Delta}{3\hbar} & 0 & 0 & 0 & 0 & -\mathrm{i}K/\hbar\\
\mathrm{i}K/\hbar & 0 & -\mathrm{i}K/\hbar & 0 & -\Gamma_\uparrow-\dfrac{\mathrm{i}\Delta}{3\hbar} & 0 & -\mathrm{i}J/\hbar & 0 & 0\\
-\mathrm{i}J/\hbar & \mathrm{i}J/\hbar & 0 & 0 & 0 & k-\dfrac{\mathrm{i}\Delta}{3\hbar} & \mathrm{i}K/\hbar & 0 & 0\\
0 & 0 & 0 & 0 & -\mathrm{i}J/\hbar & \mathrm{i}K/\hbar & k+\dfrac{\mathrm{i}\Delta}{3\hbar} & 0 & 0\\
-\mathrm{i}K/\hbar & 0 & \mathrm{i}K/\hbar & 0 & 0 & 0 & 0 & -\Gamma_\uparrow+\dfrac{\mathrm{i}\Delta}{3\hbar} & \mathrm{i}J/\hbar\\
0 & 0 & 0 & -\mathrm{i}K\hbar & 0 & 0 & 0 & \mathrm{i}J/\hbar & k^*-\dfrac{\mathrm{i}\Delta}{3\hbar}
\end{pmatrix}. \tag{31}$$

As for the block $\mathcal{C}$, it reads as $\mathcal{B}$ except for the interchange $\Gamma_\uparrow \leftrightarrow \Gamma_\downarrow$.

Ignoring for simplicity our screw molecular chain, the form of all the matrices in (29) is *exactly* the same as, e.g., that one that we would get from the stochastic Liouville equation SLE [17] provided, however, that (as so far assumed) $H''_{\mathrm{S-B}}$ is neglected and $H'_{\mathrm{S-B}}$ is replaced by a proper stochastic (e.g. Gaussian delta-correlated) potential field acting on the central system. The only difference between our form of the $\mathcal{A}$–$\mathcal{D}$ blocks and that of the same matrices in the corresponding SLE theory is dictated by physics of the problem: Namely, in contrast to the SLE approach, spontaneous processes with respect to the bath naturally appear in our fully quantum model ($H'_{\mathrm{S-B}}$ is, in our case, a coupling to a genuine *quantum* bath). Thus, $\Gamma_\uparrow <$ or even $\ll \Gamma_\downarrow$ in our model. (In any SLE theory, $\Gamma_\uparrow = \Gamma_\downarrow$ because of lack of the spontaneous processes.) This inequality really results here from the above calculations in the same way as in any other calculation taking the quantum character of the bath properly into account.

Now the last point is how to include the second term $H''_{\mathrm{S-B}}$ of $H_{\mathrm{S-B}}$. The resulting additive contributions in the above equations can be easily guessed from, e.g., the correspondence with the stochastic Liouville equation model [17]: Nothing but an additional dephasing appears in (29) what means that terms $-2\Gamma_{-1,0}$ should be added to 44 and 66 elements of $\mathcal{A}$ and $\mathcal{D}$, $-2\Gamma_{-1,1}$ should be added to 55 and 88 elements of $\mathcal{A}$ and $\mathcal{D}$, and similarly $-2\Gamma_{0,1}$ should be added to 77 and 99 elements of $\mathcal{A}$ and $\mathcal{D}$. That is what we shall automatically assume everywhere below. In [7], all these three terms $-2\Gamma_{mn}$ (see (8)) were supposed to have the same value -2Γ.

IV Special cases

Equations (29–31) are exactly those derived in [5–7]. Their numerical solution was shown there to yield that the above system violates the second law, working

as a real perpetuum mobile of the second kind. This conclusion was based on the analysis of the mean particle flow $-1 \leftrightarrow 0 \leftrightarrow +1 \leftrightarrow -1$ etc. that is responsible, via the motion of the particle along the thread of the screw molecule, for an increase of the energy of this screw molecule. Derivation of equations (29–31) in [5–7] was, however, more complicated and required details of the not fully standard Tokuyama–Mori theory [14]. This theory was fully avoided here. As the final conclusions are, however, the same, we mention here just two special cases.

– For the energy gain of the screw molecule per unit time, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}E = \frac{\mathrm{i}}{\hbar}\left\langle\left[H, \frac{\Delta}{3}\sum_{m=-1}^{+1}\sum_{\iota}(3\iota+m)c^{\dagger}_{m,\iota}c_{m,\iota}\right]\right\rangle$$

$$\approx \frac{\Delta}{3\hbar}\{K\cdot\Im\mathrm{m}(\rho_{1u,-1u}+\rho_{1d,-1d})+I\cdot\Im\mathrm{m}\rho_{0u,1u}+J\cdot\Im\mathrm{m}\rho_{-1d,0d}\}. \quad (32)$$

In the approximate equality, we have again used a smooth dependence of the density matrix elements $\mathrm{Tr}[\rho(0)(c^{\dagger}_{n,\iota}c_{m,\iota'})(t)\otimes(|\gamma\rangle\langle\alpha|)(t)]$ on indices ι, ι' of the thread. Energy gain (32) was studied numerically [5–7]. In the stationary state, it was found nonzero and positive what confirms our interpretation of the activity of our system as that of the perpetuum mobile of the second kind. Explanation and description, in physical terms, of its activity were given above.

– One very instructive example illustrating why the above system behaves as argued is provided by the situation when we break the cycle putting $K = 0$. If the above picture is correct, one should expect that the particle gets finally prevailingly localized at site '+1', having no possibility to continue further on. Notice that for $\Delta > 0$, this is the site with the highest site-energy. As for the central system, it should turn prevailingly to state $|d\rangle$. This conclusion can be easily confirmed analytically: For temperatures $T \ll \epsilon/k_{\mathrm{B}}$, $\Gamma_{\uparrow}$ becomes completely negligible (compare (5)). Omitting it completely allows one to check analytically that stationary solution to (29) reads as $\rho_{1d,1d} = 1$, with all other matrix elements $\rho_{m\alpha,n\gamma} = 0$. Already this fact contradicts basic principles of the usual equilibrium statistical thermodynamics.

As for high-temperature (i.e. classical) limit $T \gg \epsilon/k_{\mathrm{B}}$, the system may be easily argued to cease its activity as described above. The central system becomes completely decoupled from the particle, with occupation probabilities of both its states $|u\rangle$ and $|d\rangle$ turning to ≈ 0.5. So the "gate" not allowing the particle to return on the thread becomes inactive and in the infinite temperature limit, the particle becomes homogeneously distributed on the circle $\rho_{mm} = \rho_{mu,mu} + \rho_{md,md} \approx 1/3$. Also this may be analytically checked from (29).

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