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# The validity of quantum–classical multi-channel diffusion equations describing interlevel transitions in the condensed phase. The adiabatic representation

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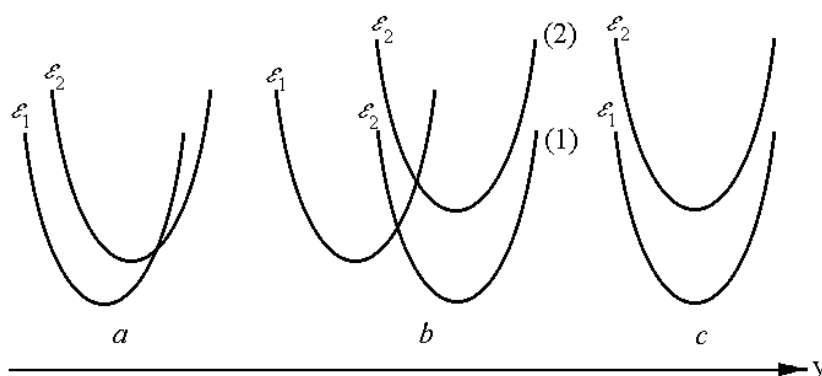
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## Abstract

We develop an approach for derivation of quantum–classical relaxation equations for a two-channel problem. The treatment is based on the adiabatic channel wavefunctions and the system–bath coupling is modelled as a bilinear interaction in momentum representation. In the quantum–classical limit we obtain Liouville equations with the relaxation operator containing diffusion terms diagonal in Liouvillian space and the off-diagonal part which is responsible for thermal interlevel transitions. The high-frequency interlevel quantum beats are fully taken into account in this relaxation term. In the framework of the present formulation and as a consequence of the momentum-dependent interaction the Smoluchovsky diffusion limit can be reached without invoking Fokker–Planck equations as an intermediate step. The inherent property of equations so obtained is that the partial rates of interlevel transitions obey the principle of detailed balance. This result could not be gained in earlier treatments of the two-level diffusion problem.

## 1. Introduction

In the present work we study the scope of validity of two-state diffusion equations (TSDEs) which are frequently used to describe nonadiabatic interlevel transitions in molecular systems immersed in a condensed medium. Most familiar are their implementations for electron transfer (ET) reactions in polar solvent [1–4]; an application to proton transfer (PT) has been also discussed recently [5]. A representative model to be considered comprises a pair of energy profiles extended over a coordinate which imitates the solute and is henceforth denoted as  $y$ . The dynamics of  $y$  is classical on each energy curve; however, quantum transitions between two levels are promoted by the nonadiabatic coupling denoted as  $V$ . The classical coordinate  $y$  is bilinearly coupled to an ensemble of harmonic oscillators which represents medium dynamics;



**Figure 1.** Typical cases of interlevel transitions. The transition occurs between energy profiles  $\varepsilon_1$  and  $\varepsilon_2$ ;  $\Delta = \varepsilon_2 - \varepsilon_1$  is the level separation. (a) The ‘inverted’ case. (b) The ‘normal’ case; the two versions (1) and (2) for  $\varepsilon_2$  correspond to exothermic and endothermic reactions. (c) The ‘resonance’ case (no relative shift of equilibrium positions of curves  $\varepsilon_1$  and  $\varepsilon_2$ ). For harmonic potentials with the same curvature  $\Delta$  is constant for case (c). Cases (a) and (b) correspond to the diabatic representation. We retain for brevity the same notation  $\varepsilon_i$  ( $i = 1, 2$ ) for diabatic and adiabatic energy profiles.

this interaction results in friction effects. Typical examples are displayed in figure 1; they correspond either to ‘spectroscopic’ (mainly vertical) transitions (figure 1(a)) or to ‘chemical’ (horizontal) transitions (figure 1(b)). These processes are often referred to as ‘inverted’ and ‘normal’ cases in the ET theory. The energy level separation  $\Delta$  and nonadiabatic coupling  $V$  are both  $y$  dependent; the simplest example with constant  $\Delta$  (a particular case of figure 1(a)) is shown in figure 1(c). This is the so-called ‘resonance level model’ [5].

The TSDE can be formulated in both diabatic and adiabatic representations. In the recent literature, the derivations and applications have been almost exclusively addressed to the diabatic case whereas our present work is devoted to the adiabatic theory. In this introductory discussion the notational discrimination between the two cases is not essential and we use the same notation  $\varepsilon_i$  ( $i = 1, 2$ ) and  $\Delta = \varepsilon_2 - \varepsilon_1$  for both adiabatic and diabatic energy profiles.

A derivation of TSDE from the microscopic-level description can be performed in terms of different techniques. The schemes of reasoning reported in the literature include the path-integral analysis of the influence functional approach [6], the decoupling of the hierarchy of kinetic equations [7, 8], the quantum–classical reduction within the Redfield formulation of the quantum relaxation theory [9] and a stochastization of the conventional quasiclassical trajectory approach of the gas phase theory of nonadiabatic transitions [10, 11]. In any case, the reduction is not at all rigorous. It actually suggests a set of approximations that trace a guideline along which the coupled diffusion dynamics could emerge from a fully quantum mechanical original model. This situation is in a striking contrast with the one-channel (a single state) case where a rigorous one-to-one correspondence between the underlying physical model and the diffusion (Fokker–Planck) equation is well known [12, 13].

Recently, the validity of this TSDE was called into question [14, 15]. The promoting argument referred to an unphysical behaviour of the transition element  $\rho_{12}$  of the reduced density matrix  $\rho$  for variable  $y$ . It was observed within a short time interval ( $0 < t < \hbar/k_B T$ ) for a specially constructed, rather artificial, model case. The pathologic effect is especially visible when the gap  $\Delta$  between the energy levels is large in the transition region. This seriously questions the possibility of a classical diffusion description of quantum variable  $\rho_{12}$ .

This comment can be relaxed by a counterargument [5] that it is a much longer timescale, governing the evolution of level populations  $\rho_{11}$  and  $\rho_{22}$ , which really matters. The fast

transition dynamics, i.e. the quantum beats of  $\rho_{12}$  at the frequency  $\omega_0 = \Delta/\hbar$ , is smeared [16] by a standard stationary condition  $\frac{d\rho_{12}}{dt} = 0$  which adjusts the average motion of fast variable  $\rho_{12}$  to a slow evolution of level populations. The unphysical trends become unobservable on a coarse-grained timescale of the population dynamics.

The problems with multi-channel diffusion equations are not, however, fully resolved by this notion. Actually, no satisfactory proofs that fundamental properties of reduced density matrix  $\rho$  cannot be violated in a TSDE have been presented. The kinetic regime with high-frequency quantum beats ( $\hbar\omega_0 \gg k_B T$ ) seems to be especially dangerous. It pertains to transitions proceeding far away from the cross-point of diabatic energy levels [5]. In a conventional TSDE, there appear three parameters having the dimension of frequency, namely,  $\omega_0$ ,  $\omega_{tr} = \frac{|V|}{\hbar}$  (the transition frequency) and  $\eta$  (the friction coefficient which measures the coupling strength between classical coordinate  $y$  and its environment). The case

$$\frac{\eta}{\omega_{tr}} \gg 1; \quad \frac{\omega_0}{\omega_{tr}} \gg 1; \quad \frac{\omega_0}{\eta} \gg 1 \quad (1.1)$$

is typical, for instance, for PT systems. An inspection of whether the quantum–classical diffusion equations are valid within this range of parameters is quite necessary.

Several observations signaled that the situation is hardly satisfactory. Most obvious is the violation of the detailed balance in TSDE [5, 17]. This effect is immediately recognized for large  $\omega_0$  ( $\frac{\hbar\omega_0}{k_B T} \gg 1$ ). Nonadiabatic transitions due to dynamic coupling  $V$  cannot provide the detailed balance in TSDE. An alternative (complementary) thermal transition mechanism is expected to exist but it has not been revealed so far. Secondly, unphysical (negative) dynamical transition rates cannot be avoided in endothermic ET reactions (a special case of figure 1(b)) [15]. Finally, we add here a third comment concerning a derivation of multi-channel Smoluchovsky equations. They were conventionally deduced [6, 9] from the original coupled Fokker–Planck equations in the overdamped kinetic limit, when the friction coefficient  $\eta$  is implied to be the largest quantity having dimension of frequency in a given system [18]. This condition is certainly violated in equation (1.1), thus questioning the two-channel Smoluchovsky approximation.

All these ambiguities motivated our present study. We reconsidered a derivation of the TSDE from the basic equation of the quantum relaxation theory [19–21]:

$$\frac{\partial \rho}{\partial t} = \frac{1}{\hbar} [h, \rho] + \hat{K} \rho. \quad (1.2)$$

Here  $h$  is the solute Hamiltonian, the brackets mean a commutator and  $\hat{K}$  represents the relaxation integral operator responsible for the solute–medium interaction. The main conclusions of this analysis are as follows. It is not the quantum–classical approximation [22] that causes the problems. The main reason arises at the stage of a derivation of the Smoluchovsky limit for multi-channel Fokker–Planck equations. The standard reasoning [6, 9] is strongly restricted here by the condition [9]  $\omega_0 \ll \eta$  and becomes invalid when it is violated. Another problem lies in the perturbation theory that is actually invoked at the stage of derivation of the relaxation operator. The system/medium interaction is conventionally taken as a bilinear form  $h_{yQ} \propto yQ$  where  $y$  represents the classical reaction coordinate and  $Q$  is a collection of bath variables. A consistent perturbational treatment of this term is only possible when a transition is well localized at the cross-point of diabatic energy levels. It may become invalid for the perturbations extended over  $y$  as revealed for the case of the ‘normal’ ET (figure 1(b)) [15], when diabatic energy levels are strongly mutually shifted along the reaction coordinate. The choice of the zero-order approximation becomes of crucial importance in this case. We found two conditions assuring a consistency of the perturbational approach. Firstly, a special separation of the total system into a dynamical subsystem (the solute) and

the environment is obligatory. It is provided by redefining the bath oscillator coordinates so as to be adjusted for a motion of the classical solute variable  $y$ . The second obligatory condition requires an adiabatic representation for the quantum two-state variable. Considering perturbationally the solute/environment interaction in a zero-order system prepared according to this prescription the detailed balance is regenerated; the other problems disappear as well. This distinguished representation has not been considered before; its formulation is the main novelty of the present study.

Manipulation with Liouville matrices, which is an essence of the work with equation (1.2), requires lengthy and tedious transformations. This determined the style of the further presentation. For the sake of clarity, we separated this technical part from the general scheme of reasoning outlined in sections 2–9. The details are briefly followed in appendices A–D.

## 2. The condition restoring the detailed balance

The problem of quantum–classical reduction of the equation of motion arises in systems with two highly anisotropic dynamical timescales. We consider the Hamiltonian  $H_{xy}$  for a combination of quantum (fast) and classical (slow) variables  $x$  and  $y$ :

$$H_{xy} = h_x + h_y + h_{xy}. \quad (2.1)$$

Here  $h_x$  and  $h_y$  depend only on  $x$ ,  $\frac{\partial}{\partial x}$  and  $y$ ,  $\frac{\partial}{\partial y}$  respectively;  $h_{xy}$  represents the interaction. The classical limit transition for  $y$  will be made as the next step. The dynamical system  $(x, y)$  interacts with the environment composed of harmonic medium modes  $Q_v : Q = \{Q_v\}$  with the bath Hamiltonian  $H_Q$ . The total (system + medium) Hamiltonian is

$$H_{xyQ} = H_{xy} + h_Q + h_{xyQ}. \quad (2.2)$$

The interaction  $h_{xyQ}$  is bilinear,

$$h_{xyQ} = \Lambda_{xy} \Phi_Q \quad (2.3)$$

where  $\Phi_Q$  is a linear combination of medium operators ( $Q_v$  or  $\frac{\partial}{\partial Q_v}$ ) as specified below.

We separate variable  $x$  and consider corresponding eigenfunctions  $\varphi_i$  and eigenvalues  $\varepsilon_i$ :

$$(h_x + h_{xy})\varphi_i = \varepsilon_i \varphi_i. \quad (2.4)$$

The Schrödinger equation (2.4) defines the  $y$ -dependent adiabatic representation:

$$\varphi_i = \varphi_i(x|y); \quad \varepsilon_i = \varepsilon_i(y).$$

The first step towards quantum–classical equations suggests averaging (i.e. integration over  $x$ ) the equation (2.1) with functions  $\varphi_i(x|y)$ . Consider a two-level model with  $i, j = 1, 2$  and focus on the operator  $\Lambda_{xy}$  in the coupling term (2.3). After averaging it converts into  $2 \times 2$  matrix

$$\Lambda = \begin{pmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{pmatrix}. \quad (2.5)$$

The matrix elements depend on  $y$  and/or  $\frac{\partial}{\partial y}$ :

$$\Lambda_{ij} = \langle \varphi_j | \Lambda_{xy} | \varphi_i \rangle \quad (2.6)$$

where  $\langle \dots \rangle$  means integration over  $x$ .

A necessary condition that the relaxation operator  $\hat{K}$  in equation (1.2) contained the terms responsible for the detailed balance can be formulated as

$$\Lambda_{12} \neq 0, \quad \Lambda_{21} \neq 0. \quad (2.7)$$

This conclusion follows from an inspection of the derivation of the thermal equilibrium conditions from the quantum relaxation theory based on equation (1.2) [19–21]; the present work suggests an explicit implementation of such an analysis. Matrix elements (2.7) always vanished in earlier studies of multi-channel quantum–classical equations.

### 3. The solute/bath interaction

The structure of relaxation operator  $\hat{K}$  in equation (1.2) is determined by the form of interaction operator  $\Lambda_{xy}$ . The model where  $\Lambda_{xy}$  is  $x$  independent introduces a significant simplification and produces a realistic background for applications. In conventional theories  $\Lambda_{xy} = y$ . Here we assume

$$\Lambda_{xy} \rightarrow \Lambda_y = -i\hbar \frac{\partial}{\partial y}. \quad (3.1)$$

The explanation of how the expression (3.1) can arise is suggested below. This assumption results in the following structure of matrix  $\Lambda$ :

$$\Lambda = \Lambda_1 + \Lambda_2$$

$$\Lambda_1 = -i\hbar \frac{\partial}{\partial y} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \Lambda_2 = -i\hbar J \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (3.2)$$

where the coupling term is

$$J(y) = \langle \varphi_1 | \frac{\partial}{\partial y} | \varphi_2 \rangle = \frac{\langle \varphi_1 | \frac{\partial W_{xy}}{\partial y} | \varphi_2 \rangle}{\varepsilon_2 - \varepsilon_1}. \quad (3.3)$$

We imply that the interaction in equation (2.1) is a potential term:  $h_{xy} = W_{xy} = W(x, y)$ .

In the diabatic representation ( $y$ -independent  $\varphi_i(x)$ ) no coupling can be inserted in matrix  $\Lambda$ . Both necessary conditions, i.e. the form (3.1) of the system–bath interaction and the adiabatic representation, have never been satisfied in earlier studies; this was followed by an immediate consequence of a violation of conditions (2.7).

### 4. The shifted bath oscillators as natural environment variables

Originally, the variables  $y$  (the slow dynamical coordinate),  $q_v$  (the bath) and their interaction are defined in terms of the Hamiltonian

$$H_{yq} = h_y + h_q + h_{yq} \quad (4.1)$$

where  $h_q$  represents a standard ensemble of purely oscillatory modes  $q_v$  with masses  $m_v$  and frequencies  $\omega_v$ . The bilinear interaction is defined as

$$h_{yq} = y \sum_v c_v q_v \quad (4.2)$$

where  $c_v$  are coupling amplitudes. A standard procedure transforms this interaction by shifting the equilibrium positions of bath oscillators as

$$Q_v = q_v - q_{0v}$$

$$q_{0v} = -y \frac{c_v}{m_v \omega_v^2}. \quad (4.3)$$

Usually, this procedure is performed with a harmonic potential for the system coordinate  $y$  [12, 13, 23, 24]; then  $y$  is involved in the transformation (4.3) resulting in the corresponding shift of its equilibrium position (the spin-boson model). The novel element of the present approach is that we do not change  $y$  but treat shifted modes  $Q_v$  as modified bath variables adjusted to  $y$ . On the other hand, as compared to the one-channel stochastic approach [12, 13], the change of variables  $q_v \rightarrow Q_v$  is an essential novelty. Such a change is unnecessary in one-channel applications, when transformation of the dynamic equation to the GLE form is exact [25, 26]. In our multi-channel case a modified bath formulation is a necessary ingredient of the proper zero-order approximation underlying the second-order Redfield equation (1.2).

The change of variables results in the following modification of Hamiltonian (4.1):

$$H_{yq} \rightarrow H_{yQ} = h_y + h_Q + h_{yQ}. \quad (4.4)$$

Here  $h_y$  is modified by adding an extra potential term (we do not change the notation for brevity):

$$h_y \rightarrow h_y - \frac{1}{2}y^2 \sum_v \frac{c_v^2}{m_v \omega_v^2}. \quad (4.5)$$

Coordinates  $Q_v$  are coupled via kinetic energy (see appendix A). Diagonalization of the pertaining bath Hamiltonian provides the new oscillator variables and the new bath frequency spectrum. We imply this procedure to be performed but retain for brevity the same notations  $Q_v$  and  $\omega_v$  for the transformed bath modes and frequencies. With this contracted notation we find the remaining components of equation (4.4) as

$$\begin{aligned} h_Q &= \sum_v -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_v^2} + \frac{\omega_v^2}{2} Q_v^2 \\ h_{yQ} &= -i\hbar \frac{\partial}{\partial y} \sum_v \gamma_v \left( -i\hbar \frac{\partial}{\partial Q_v} \right). \end{aligned} \quad (4.6)$$

The frequency spectrum and the spectral density are now modified as compared to the original bath due to the diagonalization procedure. The new interaction amplitudes  $\gamma_v$  can be explicitly expressed in terms of  $c_v$  and other parameters of the original Hamiltonian (4.1), see appendix A for details.

Equations (4.4)–(4.6) constitute a background for the basic Hamiltonian (2.2), (2.3). Its most essential feature is the form (4.6) of the solute/bath interaction: just the same as required in order to regenerate the detailed balance.

For the bath Hamiltonian and the interaction as given by equation (4.6) we shall further need the correlation function,

$$\mathcal{K}(\tau) = \sum_{vv'} \frac{e^{-\varepsilon_v/k_B T}}{Z} \langle v | \Phi_Q | v' \rangle \langle v' | \Phi_Q | v \rangle \exp \left[ -\frac{i\tau}{\hbar} (\varepsilon_v - \varepsilon'_v) \right] \quad (4.7)$$

where  $\varepsilon_v = \hbar\omega_v$ ,  $Z$  is the partition function, oscillator states are denoted as  $|v\rangle$  and  $|v'\rangle$  and

$$\Phi_Q = \sum_v \gamma_v \left( -i\hbar \frac{\partial}{\partial Q_v} \right). \quad (4.8)$$

All results will be expressed in terms of the two related correlation functions,

$$\begin{aligned} \mathcal{K}_+(\tau) &= (1/2)[\mathcal{K}(\tau) + \mathcal{K}(-\tau)] \\ \mathcal{K}_-(\tau) &= (1/2)[\mathcal{K}(\tau) - \mathcal{K}(-\tau)] \end{aligned} \quad (4.9)$$

which are available in a conventional form

$$\begin{aligned} \mathcal{K}_+(\tau) &= \sum_v \gamma_v^2 \frac{\hbar\omega_v}{2} \coth \frac{\hbar\omega_v}{2k_B T} \cos \omega_v \tau \\ \mathcal{K}_-(\tau) &= i \sum_v \gamma_v^2 \frac{\hbar\omega_v}{2} \sin \omega_v \tau. \end{aligned} \quad (4.10)$$

## 5. The dynamical evolution of the adiabatic two-level system

We considered the dynamical equation without the relaxation term that has the form

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} [h, \rho] = \frac{1}{i\hbar} L[h]\rho \quad (5.1)$$

where  $L[h]$  is the  $4 \times 4$  Liouvillian commutation matrix. The adiabatic two-state Hamiltonian  $h$  is represented as

$$h = \begin{pmatrix} \frac{\hat{p}^2}{2m} + \varepsilon_1(y) & \frac{\hbar}{i} u J \\ -\frac{\hbar}{i} u J & \frac{\hat{p}^2}{2m} + \varepsilon_2(y) \end{pmatrix}. \tag{5.2}$$

Here  $\varepsilon_1, \varepsilon_2$  represent adiabatic energy levels, coupling matrix element  $J$  is defined in equation (3.3),  $u = p/m$  is the velocity where  $p = p_y$  represents the classical momentum. The momentum operator  $\hat{p}$  reduces to  $p$  in the classical limit; in this case the operator matrix (5.2) reduces to the ordinary matrix  $h^c$ :

$$h \rightarrow h^c. \tag{5.3}$$

For a general case the quantum–classical reduction rules are summarized in appendix B. The quantum mechanical operator  $A$  is converted into matrix  $A^c$ , composed of classical variables, similar to the reduction in equation (5.3). The commutation ( $L$ ) and anticommutation ( $M$ ) operations with  $A$  reduce to the following operations performed with  $A^c$ :

$$\begin{aligned} L[A] &\Rightarrow L[A^c] - \frac{i\hbar}{2} \mathcal{L}[A^c] \\ M[A] &\Rightarrow M[A^c] - \frac{i\hbar}{2} \mathcal{M}[A^c]. \end{aligned} \tag{5.4}$$

On the right-hand side  $\mathcal{L}[\dots]$  and  $\mathcal{M}[\dots]$  represent the corresponding commutation and anticommutation Liouvillian matrices composed of Poisson brackets involving the elements of  $A^c$  as one of their components. The algorithm for explicitly performing operations  $\mathcal{L}$  and  $\mathcal{M}$  is formulated in appendix B. It is straightforward to show that  $L = 0$  and  $M = 0$ , when  $A$  is proportional to the unit matrix:  $A = aI$  where  $a$  represents a scalar number or operator.

The solution to equation (5.1) is formally expressed in terms of the propagator

$$R(\tau) = \exp\left\{-\frac{i\tau}{\hbar} L[h]\right\}. \tag{5.5}$$

The well known expression for  $L[h]$  [22] reads

$$L[h] = L[h^c] + i\hbar \left(-u \frac{\partial}{\partial y} + B \frac{\partial}{\partial p}\right) \tag{5.6}$$

where, for the present adiabatic case,

$$L[h^c] = i\hbar \begin{pmatrix} 0 & -uJ & -uJ & 0 \\ uJ & i\omega_0 & 0 & -uJ \\ uJ & 0 & -i\omega_0 & -uJ \\ 0 & uJ & uJ & 0 \end{pmatrix} \tag{5.7}$$

$$B = \begin{pmatrix} \varepsilon'_1 & 0 & 0 & 0 \\ 0 & \frac{1}{2}(\varepsilon'_1 + \varepsilon'_2) & 0 & 0 \\ 0 & 0 & \frac{1}{2}(\varepsilon'_1 + \varepsilon'_2) & 0 \\ 0 & 0 & 0 & \varepsilon'_2 \end{pmatrix} + O(\hbar). \tag{5.8}$$

Here  $\omega_0 = \Delta/\hbar = (\varepsilon_2 - \varepsilon_1)/\hbar$  and ‘ $\prime$ ’ means  $\frac{d}{dy}$ . The off-diagonal elements of matrix  $B$  have a higher order in  $\hbar$ . They vanish after the classical limit transition  $\hbar \rightarrow 0$  and are not specified here. Hence, the diagonal Poisson-bracket terms in equation (5.6) represent the classical evolution along the trajectories governed by adiabatic potentials as suggested by equation (5.8).



For the case when only the diagonal part of matrix  $L[h^c]$  is retained in equation (5.6) we obtain the propagator

$$R_0(\tau) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{i\tau\omega_0} & 0 & 0 \\ 0 & 0 & e^{-i\tau\omega_0} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (5.9)$$

It contains high-frequency quantum beats between adiabatic levels (we focus on the case of large  $\omega_0$ ). By using the interaction representation, i.e. by assuming

$$R(\tau) = R_0(\tau)R_1(\tau) \quad (5.10)$$

and substituting equation (5.10) in (5.5) one can conventionally find the equation determining  $R_1(\tau)$ . We introduce now timescales associated with different kinds of motion:

$$\begin{aligned} \tau_{cl} &= \frac{1}{\omega_{cl}} && \text{(the motion on classical trajectories)} \\ \tau_{tr} &= \frac{1}{uJ_0} && \text{(the nonadiabatic transitions)} \\ \tau_{beats} &= \frac{1}{\omega_0} && \text{(the quantum beats)}. \end{aligned} \quad (5.11)$$

Here  $\omega_{cl}$  denotes a characteristic frequency for the classical  $y$ -motion and coupling  $J(y)$  is taken as  $J(y) = J_0 + J_1(y) + \dots$ . Provided there exists a hierarchy of timescales obeying

$$\tau_{beats} \ll \tau_{cl}, \tau_{tr} \quad (5.12)$$

we can conclude that for short time periods  $t$  satisfying

$$\tau_{beats} \ll t \ll \tau_{cl}, \tau_{tr} \quad (5.13)$$

one can assume  $R_1(\tau) \approx 1$  and

$$R(\tau) \approx R_0(\tau). \quad (5.14)$$

This notion opens a way for the incorporation of quantum beats in the relaxation operator as derived in appendix C.

## 6. The relaxation operator

The relaxation operator  $\hat{K}$  of the basic equation (1.2) is defined by the expression

$$\hat{K}\rho = -\frac{1}{\hbar^2} \int_0^t \bar{K}(\tau)\rho(t-\tau) d\tau. \quad (6.1)$$

The general expression for the kernel  $\bar{K}(\tau)$  has been earlier derived [9] in the form

$$\bar{K}(\tau) = \mathcal{K}_+(\tau)L[\Lambda]R(\tau)L[\Lambda] - \mathcal{K}_-(\tau)L[\Lambda]R(\tau)M[\Lambda] \quad (6.2)$$

where  $L[\Lambda]$  and  $M[\Lambda]$  represent commutation and anticommutation operations with the interaction operator  $\Lambda = \Lambda_y$ . In the quantum-classical limit they reduce to operations involving matrix  $\Lambda^c$  as described by equations (5.4). Correlation functions  $\mathcal{K}_\pm(\tau)$  are defined in equation (4.10).

The expression for  $\Lambda^c$  is a classical limit of equation (3.2):

$$\begin{aligned} \Lambda^c &= \Lambda_1 + \Lambda_2 \\ \Lambda_1 &= p_y \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \Lambda_2 = -i\hbar J \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \end{aligned} \quad (6.3)$$

The expressions to be inserted into equation (6.2) are

$$\begin{aligned} \mathcal{L}[\Lambda_1] &= -i\hbar \frac{\partial}{\partial y} \equiv L_1 \\ M[\Lambda_1] &= 2p_y \equiv M_1 \\ L[\Lambda_1] &= \mathcal{M}[\Lambda_1] = 0. \end{aligned} \quad (6.4)$$

These results arise in terms of prescription (5.4) as applied to the diagonal part  $\Lambda_1$  of operator  $\Lambda$ . Additionally, by operating with its off-diagonal part  $\Lambda_2$ , we obtain Liouvillian matrices corresponding to matrix commutations and anticommutations (the terms  $L_2$  and  $M_2$  below) and the Poisson bracket terms ( $L_3$  and  $M_3$ ):

$$\begin{aligned} L[\Lambda_2] &= L_2 + L_3 \\ L_2 &= -i\hbar J P \\ L_3 &= -i\hbar J' Q \frac{\partial}{\partial p} \end{aligned} \quad (6.5)$$

$$\begin{aligned} M[\Lambda_2] &= M_2 + M_3 \\ M_2 &= -i\hbar J Q \\ M_3 &= \frac{\hbar^2}{2} J' P \frac{\partial}{\partial p}. \end{aligned} \quad (6.6)$$

Here two matrices are introduced:

$$P = \begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix}; \quad Q = \begin{pmatrix} 0 & -1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ -1 & 0 & 0 & -1 \\ 0 & -1 & 1 & 0 \end{pmatrix}. \quad (6.7)$$

Altogether, the quantum–classical expressions for  $L[\Lambda]$  and  $M[\Lambda]$  to be inserted in equation (6.2) are

$$\begin{aligned} L[\Lambda] &= L_1 + L_2 + L_3 \\ M[\Lambda] &= M_1 + M_2 + M_3. \end{aligned} \quad (6.8)$$

This is a result of an accurate quantum–classical reduction. In order to obtain the coupled diffusion equations in a tractable form, a set of further approximations is required, which retain ‘essential’ and drop away ‘inessential’ terms in equation (6.2). The underlying analysis is transferred to appendix C.

## 7. The two-channel diffusion equations

The quantum–classical relaxation equations that follow if we select according to appendix C important contributions to the relaxation operator have the form

$$\begin{aligned} \frac{\partial \rho_{11}}{\partial t} &= N_{11} \rho_{11} + uJ(\rho_{12} + \rho_{21}) - J^2 D(\omega_0) \rho_{11} + J^2 D(-\omega_0) \rho_{22} \\ \frac{\partial \rho_{12}}{\partial t} &= N_{12} \rho_{12} + i\omega_0 \rho_{12} + uJ(\rho_{11} - \rho_{22}) - 2J^2 [D_0 \rho_{12} + D_+(2\omega_0) \rho_{21}] \\ \frac{\partial \rho_{21}}{\partial t} &= N_{21} \rho_{21} - i\omega_0 \rho_{21} + uJ(\rho_{11} - \rho_{22}) - 2J^2 [D_0 \rho_{21} + D_+(-2\omega_0) \rho_{12}] \\ \frac{\partial \rho_{22}}{\partial t} &= N_{22} \rho_{22} + uJ(\rho_{12} + \rho_{21}) + J^2 D(\omega_0) \rho_{11} - J^2 D(-\omega_0) \rho_{22}. \end{aligned} \quad (7.1)$$

The following definitions and notations are accepted:

$$N_{ij} = D_0 \frac{\partial}{\partial y} \left[ \frac{\partial}{\partial y} + \frac{1}{k_B T} \frac{\varepsilon'_i + \varepsilon'_j}{2} \right] - u \frac{\partial}{\partial y} + \frac{\varepsilon'_i + \varepsilon'_j}{2m} \frac{\partial}{\partial u} \quad (7.2)$$

$$D(\omega) = \int_0^\infty d\tau [\mathcal{K}_+(\tau) \cos \omega\tau + \mathcal{K}_-(\tau) i \sin \omega\tau] = \frac{1}{2} \int_0^\infty d\tau [\mathcal{K}(\tau) e^{i\omega\tau} + \mathcal{K}(-\tau) e^{-i\omega\tau}]$$

$$D_+(\omega) = \int_0^\infty d\tau \mathcal{K}_+(\tau) e^{i\omega\tau} \quad (7.3)$$

$$D_0 = D(\omega = 0) = D_+(\omega = 0).$$

The comments given below are aimed at clarifying several novel features of equations (7.1).

- (a) Operators  $N_{ij}$  ( $i, j = 1, 2$ ) are diagonal in the Liouvillian space, i.e. they correspond to an independent evolution of elements  $\rho_{ij}$  of the density matrix. Their diffusion part originates from matrices  $L_1, M_1$  in equation (C.10). They generate equations for diagonal elements  $\rho_{11}, \rho_{22}$  that represent a true adiabatic evolution of a quantum–classical system. A remarkable fact is that the Smoluchovsky diffusion limit is directly reached in terms of the present formulation, without separating the Fokker–Planck equation as an intermediate step. This result is gained due to expressing the solute/environment interaction in terms of momentum operators.

Earlier derivations [6, 9] started from the bilinear coordinate-dependent interaction and resulted in multi-channel Fokker–Planck equations, with the diffusion coefficient  $D_p = m\eta k_B T$  proportional to friction coefficient  $\eta$ . As discussed in the introduction, their reduction to the Smoluchovsky limit by using standard methodologies [16, 18] is formally prohibited in the case  $(\eta/\omega_0) \leq 1$ , when  $\eta$  proves to be not the smallest parameter having dimension of frequency. The approach described in section 4 suggests a transparent way to circumvent this difficulty.

- (b) The terms proportional to  $uJ$  are responsible for purely dynamical interlevel transitions. Terms of this sort were also present in earlier multi-channel theories [2–4, 6, 9], with a modification due to the diabatic representation of channel basis functions that has been always invoked before. After eliminating off-diagonal elements of the density matrix by using the Green function technique [9, 28, 29], the coupled balance equations for  $\rho_{11}$  and  $\rho_{22}$  had been obtained. We repeat this concluding part of the derivation in the next section.
- (c) The cross-terms containing correlation functions  $D(\pm\omega_0)$  comprise direct coupling of adiabatic states promoted by the solute/bath interaction. They vanish in the diabatic representation. The partial rates of corresponding nonadiabatic transitions obey the detailed balance, because [19, 20]

$$\frac{D(\omega_0)}{D(-\omega_0)} = e^{-\hbar\omega_0/k_B T}. \quad (7.4)$$

A search for these terms was the main objective of the present work. They arise as a result of multiplications of relevant Liouvillian matrices in equation (6.2).

- (d) We recall two simplifying approximations introduced in the last part of appendix C on the way from the full expression (6.2) for the relaxation operator to equations (7.1). This are, first, the ‘resonance condition’  $\omega'_0 = 0$  which provides the simplest form for the diffusion part of operators  $N_{ij}$ . Second, the ‘interference terms’ (C.11) are neglected in the relaxation operator. The direct multiplication of Liouville matrices shows that they contribute only to nonadiabatic transitions coupling  $\rho_{ii}$  and  $\rho_{ij}$  and contain quantities proportional to  $J \frac{\partial}{\partial y}$ . On this background, it is expedient to introduce the third approximation directly in equations (7.1), which would make them more tractable.

We shall withdraw the last terms (with square brackets) from the second and third equations (7.1), determining the evolution of  $\rho_{12}$  and  $\rho_{21}$ . A rational motivation for this step could be given by the relations

$$\omega_0 \gg J^2 D_0 \gg J^2 |D_+(2\omega_0)| \tag{7.5}$$

which are expected to be valid for the case of large  $\omega_0$  we are considering here.

### 8. The balance equations

Our goal is to derive the Smoluchovsky limit of equation (7.1) under conditions providing the following hierarchy of timescales which is in accord with equations (5.11)–(5.13):

$$\omega_0 \gg \eta \gg \omega_{cl} \gg \tau_y^{-1}. \tag{8.1}$$

Here  $\eta$  denotes the friction coefficient ( $\eta^{-1}$  is the velocity relaxation period),  $\omega_{cl}$  is the characteristic frequency of the classical  $y$ -motion and  $\tau_y$  is the diffusion relaxation period. These quantities are additionally interrelated as

$$D_0 = k_B T / m \eta, \quad \eta = \tau_y \omega_{cl}^2 \tag{8.2}$$

where  $D_0$  is the diffusion constant in equation (7.2). The  $y$  dependence of  $\omega_0$  is suppressed in this simplified treatment.

The first conventional step eliminating off-diagonal elements of the density matrix in equation (7.1) is that one assumes

$$\partial \rho_{12} / \partial t = \partial \rho_{21} / \partial t = 0. \tag{8.3}$$

Provided the last terms on the right-hand sides of equations for  $\rho_{12}$  and  $\rho_{21}$  are negligible, as discussed in item (d) of section 7, these equations become uncoupled and it suffices to consider only  $\rho_{12}$ . Under conditions (8.1) there exists a time interval  $\Delta t$  which is much shorter than  $\tau_y$  but much larger than  $\omega_0^{-1}$ . Equations (8.3) are valid for  $\rho_{12}$  averaged over such an interval. The averaging eliminates the strongly oscillating (with frequency  $\omega_0$ ) component of  $\rho_{12}$  but retains its regular component evolving on the diffusion timescale.

With this preliminary, we introduce the Green operator resolving equation (8.3) for  $\rho_{12}$ :

$$G_{12} = (i\omega_0 + N_{12})^{-1} \cong (i\omega_0)^{-1} (1 - N_{12}/i\omega_0). \tag{8.4}$$

According to equation (7.2), we separate the diffusion and classical dynamic components of operator  $N_{12}$ :

$$\begin{aligned} N_{12} &= L_{12} + M_{12} \\ L_{12} &= D_0 \frac{\partial}{\partial y} \left[ \frac{\partial}{\partial y} + \frac{1}{2k_B T} (\varepsilon'_1 + \varepsilon'_2) \right] \\ M_{12} &= -u \frac{\partial}{\partial y} + \frac{1}{2m} (\varepsilon'_1 + \varepsilon'_2) \frac{\partial}{\partial u}. \end{aligned} \tag{8.5}$$

The characteristic frequency of  $N_{12}$  is  $\omega_{cl}$  and the inequality  $\omega_{cl}/\omega_0 \ll 1$  accounts for the last approximation involved in equation (8.4). The resulting expression for the regular component of  $\rho_{12}$

$$\rho_{12}(t) = -(i\omega_0)^{-1} [1 - (L_{12} + M_{12})/i\omega_0] u J[\rho_{11}(t) - \rho_{22}(t)] \tag{8.6}$$

is now inserted in the first and fourth lines of equations (7.1). Note that  $\rho_{11}(t)$  and  $\rho_{22}(t)$  are functions of  $y$  and  $u$ ; on the other hand, we suppress here for simplicity the  $y$  dependence of  $J$ , similar to the case of  $\omega_0$  as noted above. Provided only the coarse-grained diffusion timescale

( $\Delta t$  no less than the velocity relaxation period) is essential, one introduces spatial distributions  $\sigma_{11}(y, t)$  and  $\sigma_{22}(y, t)$  by assuming

$$\begin{aligned}\rho_{11}(y, u, t) &= (m/2\pi k_B T)^{1/2} \exp(-mu^2/2k_B T) \sigma_{11}(y, t) \\ \rho_{22}(y, u, t) &= (m/2\pi k_B T)^{1/2} \exp(-mu^2/2k_B T) \sigma_{22}(y, t).\end{aligned}\quad (8.7)$$

The dynamic components of operators  $N_{11}$  and  $N_{22}$  vanish after operating with the Maxwell distributions (8.7) and performing integrals over  $u$ . This procedure also eliminates dynamic operator  $M_{12}$  in equation (8.6). The simplified version of balance equations which ultimately arises under approximations (8.3), (8.4), (8.6) and (8.7) is expressed as the nonadiabatic Smoluchovsky equations

$$\begin{aligned}\partial\sigma_{11}/\partial t &= D_0 \frac{\partial}{\partial y} \left[ \frac{\partial}{\partial y} + \varepsilon'_1/k_B T \right] \sigma_{11} + J^2 [D(-\omega_0)\sigma_{22} - D(\omega_0)\sigma_{11}] \\ &\quad - \frac{2J^2 k_B T}{\omega_0^2 m} L_{12} [\sigma_{11} - \sigma_{22}]\end{aligned}\quad (8.8)$$

and the similar equation for  $\sigma_{22}$ . Here we supposed for simplicity that  $J$  does not depend on  $y$ . The nonadiabatic transitions generated by the second and third terms of equation (8.8) originate, respectively, from the thermal solute–bath interaction and from the direct dynamic interlevel interactions. It is remarkable that the dynamic term vanishes when the diffusion relaxation is completed and  $\sigma_{11}$  and  $\sigma_{22}$  become Boltzmann distributions. This is so because diffusion operator  $L_{12}$  annihilates Boltzmann distributions. This conclusion is exact provided  $\omega_0$  and  $J$  are  $y$  independent, as assumed above. Otherwise, some extra terms proportional to  $\partial\omega_0/\partial y$  and  $\partial J/\partial y$  arise which are, however, of little significance, because expressions of this sort were not treated quite accurately in other places in the present derivation (see appendix C for example). It can be stated that the quantities  $\omega_0$  and  $J$  should be treated like quasiclassical potentials which means that their commutations with operator  $\partial/\partial y$  may be neglected. Altogether, we infer that only thermal transitions seem to occur once the intralevel equilibrium is attained. On the other hand, dynamic nonadiabatic transitions are significant in a case of strongly nonequilibrium spatial level distributions.

Finally, let us discuss the different kinetic regime determined by the alternative condition to equation (8.1), namely  $\omega_0 \ll \eta$ . Under this assumption the velocity relaxation with the period  $\tau_u = \eta^{-1}$  provides the shortest timescale as compared to other processes and we can apply an approximation similar to equation (8.7) directly to  $\rho_{12}$  and  $\rho_{21}$ . Then averaging over  $u$  with Maxwell distributions annihilates the terms coupling diagonal and off-diagonal elements of the density matrix in equation (7.1). As a result, one obtains diffusion equations (8.8) without dynamic transitions (the last term of equation (8.8) is dropped). The adiabatic representation of this sort has been considered by Shushin and Tachiya [10, 11].

## 9. Discussion

The earlier work with the TSDE [1–4, 6, 13, 15, 26] was mainly addressed to a ‘normal’ ET (figure 1(b)) in a diabatic representation. Such approach is constrained by a condition that the transition state must be localized [2, 3, 13]. The alternative adiabatic treatment met some inherent problems [10, 11]. It was revived recently [11, 28–30] in the context of the ‘inverted’ ET (figure 1(a)). The present study has established a natural background for deriving adiabatic quantum–classical TSDEs in the case of delocalized interlevel transitions. It covers all examples shown in figure 1 provided the adiabatic energy gap is not too small ( $\bar{u}J/\omega_0 \ll 1$ ; here  $\bar{u}$  means the mean thermal velocity). We formulated the two conditions that are sufficient for making consistent the quantum–classical limit transition. First, the solute/medium interaction

must be expressed in terms of momenta rather than the coordinates; this description emerges when the adjusted bath model is accepted as a zero-order approximation for the second-order relaxation equation (1.2). Second, an adiabatic rather than diabatic representation of the channel (electronic) basis functions must be used. The distinguished role of the adiabatic representation for reproducing the detailed balance effect is a consequence of the interaction model introduced in section 3. The direct interaction of the fast quantum variable ( $x$ ) with thermal bath modes ( $q$ ) is disregarded. The coupling of the dynamic subsystem to the bath is performed exclusively via the slow coordinate ( $y$ ):  $h_{xyq} \rightarrow h_{xy}$ , see equation (3.1). As a result, the system-induced factor  $\Lambda$  of the bilinear interaction term becomes a diagonal matrix in a diabatic two-state representation. On the other hand, matrix  $\Lambda$  acquires its off-diagonal coupling term responsible for the detailed balance if the direct  $x/q$  interaction is introduced, irrespective of whether the basis states are diabatic or adiabatic and whether the interaction is expressed in terms of coordinates or their momenta. We preferred, however, a pure model requiring a minimum amount of input information in order to reproduce the desired effect. In fact, it naturally covers electron and PT systems and thereby has a number of applications.

The thermal transitions ensuring detailed balance are supplemented by purely dynamical transitions which can be important in the adiabatic regime until intralevel Boltzmann equilibrium is gained. Such a description seems quite relevant for the resonant case (figure 1(c)) when the transitions are located around the minima of adiabatic potentials far away from the cross-point region. For an inverted ET case (figure 1(a)) a competition between transitions of this sort and those at the cross-point should be investigated.

The present adiabatic Smoluchovsky model applies for two extreme cases when  $\omega_0$  is large ( $\omega_0/\eta \gg 1$ , equation (8.8) of the present work) or small ( $\omega_0/\eta \ll 1$ , equation (8.8) without the last ‘dynamic’ term); this approach was originally derived in [11]. Intermediate cases do not allow for a separation of timescales and thus require a complete treatment in terms of equation (7.1) involving both coordinate  $y$  and velocity  $u$ . The diabatic representation seems to be most relevant for a treatment of the avoided crossing region with a small level splitting ( $\bar{u}J/\omega_0 \gg 1$ ) and conventional procedures [2–4, 6, 13] are well adapted for this case.

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## Appendix A. The bath transformation

Consider a transformation of the Hamiltonian in equation (4.1) in terms of two sets of coordinates

$$(r_i) = (y, q_v); \quad (r'_i) = (y, Q_v) \quad i = 0, 1, \dots \quad (\text{A.1})$$

with  $r_0 = r'_0 = y$  and  $r_i = q_v, r'_i = Q_v$  for  $i = v = 1, 2, \dots$ . The metric tensor for the set ( $r'_i$ ) is defined as

$$g^{ij} = \sum_{k=0} \frac{1}{m_k} \frac{\partial r'_i}{\partial r_k} \frac{\partial r'_j}{\partial r_k} \quad (\text{A.2})$$

where  $m_0 = m$  is the mass for  $y$ . This expression becomes readily available by explicitly evaluating the derivatives in terms of equation (4.3):

$$\begin{aligned} g^{00} &= \frac{1}{m} \equiv g^{yy}; & g^{0v} &= g^{v0} = -\frac{b_v}{m} \\ g^{\mu\nu} &= \frac{1}{m} \frac{\partial Q_\mu}{\partial y} \frac{\partial Q_\nu}{\partial y} + \sum_{\lambda=1} \frac{1}{m_\lambda} \frac{\partial Q_\mu}{\partial q_\lambda} \frac{\partial Q_\nu}{\partial q_\lambda} = \frac{1}{m} b_\mu b_\nu + \frac{1}{m_\mu} \delta_{\mu\nu}. \end{aligned} \quad (\text{A.3})$$

Here the notation  $b_v = \frac{c_v}{m_v \omega_v^2}$  is introduced. This metric tensor is  $y$  independent.

Altogether, the transformation  $q_v \rightarrow Q_v$  changes the kinetic energy, the interaction and adds  $y$ -dependent terms to the bath oscillator potentials. The latter contributions renormalize the solute potential according to equation (4.5) [25]. The remaining components of Hamiltonian (4.1) change as

$$\begin{aligned} h_q + h_{yq} &\rightarrow h_Q + h_{yQ} \\ h_Q &= \sum_{\mu\nu} -\frac{\hbar^2}{2M_{\mu\nu}} \frac{\partial}{\partial Q_\mu} \frac{\partial}{\partial Q_\nu} + \sum_\nu \frac{m_\nu \omega_\nu^2}{2} Q_\nu^2 \\ h_{yQ} &= -i\hbar \frac{\partial}{\partial y} \sum_\nu \frac{b_\nu}{m} \left( -i\hbar \frac{\partial}{\partial Q_\nu} \right). \end{aligned} \quad (\text{A.4})$$

They are now expressed in terms of the parameters of the metric tensor (A.3), namely  $b_\nu$  and

$$\frac{1}{M_{\mu\nu}} = \frac{1}{m_\nu} \delta_{\mu\nu} + \frac{1}{m} b_\mu b_\nu. \quad (\text{A.5})$$

The final step is a trivial diagonalization of the bath Hamiltonian  $h_Q$  which yields equation (4.6) with new normal modes  $Q_\nu$  and their new frequencies  $\omega_\nu$  (the notation is not changed for brevity). This procedure is unnecessary to specify in the present context; it will be specially considered elsewhere.

## Appendix B. Quantum–classical expressions for commutations and anticommutations

Let matrix elements  $a_{ij}$  and  $b_{ij}$  of matrices  $A$  and  $B$  be quantum mechanical quantities, composed of coordinate ( $y$ ) and momentum ( $p_y = -i\hbar \frac{\partial}{\partial y}$ ) operators. In the classical limit they convert into  $a_{ij}^c$  and  $b_{ij}^c$ , the same functions of the classical coordinate and momentum. The corresponding matrices are  $A^c$  and  $B^c$ . The following expressions represent classical limits for the commutation  $[\dots, \dots]_-$  and anticommutation  $[\dots, \dots]_+$  operations:

$$([A, B]_{\mp})_{ij} = ([A^c, B^c]_{\mp})_{ij} - \frac{i\hbar}{2} \sum_k \{a_{ik}^c, b_{kj}^c\} \pm \{a_{kj}^c, b_{ik}^c\}. \quad (\text{B.1})$$

Here  $\{\dots, \dots\}$  denotes Poisson brackets:

$$\{a, b\} = \frac{\partial a}{\partial p_y} \frac{\partial b}{\partial y} - \frac{\partial a}{\partial y} \frac{\partial b}{\partial p_y}.$$

The prescription (B.1) follows after properly taking the classical limit, including the first-order in  $\hbar$  terms, for operator products. These rules [22] comprise a truncated Taylor expansion based on the Wigner-transform technique. The full expansion, also called the Weyl transformation, is available in the literature [27].

## Appendix C. The simplification of the quantum–classical relaxation operator

### C.1. The local approximation

The relaxation term (6.1) can be modified by assuming [9, 15]

$$\rho(t - \tau) = R(-\tau)\rho(t). \quad (\text{C.1})$$

This approximation implies a purely dynamic evolution without relaxation. It does not violate the accuracy of equation (6.1) which was obtained as a second order of the perturbation expansion relative to the relaxation operator; any relevant correction added to equation (C.1) would contribute to a higher order of the perturbation theory.

By this means, the integral operator  $\hat{K}$  is transformed to the Liouvillian matrix  $K$ :

$$\begin{aligned} [\hat{K}\rho](t) &= K\rho(t) \\ K &= -\frac{1}{\hbar^2} \int_0^\infty \bar{K}(\tau)R(-\tau) d\tau. \end{aligned} \quad (\text{C.2})$$

The upper limit  $t = \infty$  becomes legitimate after extending the hierarchy of timescales suggested by equations (5.11), (5.12):

$$\tau_{beats} \leq \tau_{bath} \ll \tau_{cl}, \tau_{tr}. \quad (\text{C.3})$$

Here  $\tau_{bath}$  denotes the characteristic period of the bath relaxation determined by the widths of bath correlation functions. Without its left-hand part,

$$\tau_{beats} \leq \tau_{bath} \quad (\text{C.4})$$

inequality (C.3) is a standard condition eliminating non-Markovian effects from relaxation kinetics. The additional constraint (C.4) provides a background for making a change  $R(\pm\tau) \rightarrow R_0(\pm\tau)$  in the integrand of equation (C.2). This simplification is discussed at the end of section 5. It proves to be premature at the present stage but can be safely introduced after integration by parts, as described below.

### C.2. Sorting the orders of magnitude

It is now expedient to rewrite the integrand of relaxation matrix  $K$  in a more explicit form:

$$\begin{aligned} \bar{K}(\tau)R(-\tau) &= \mathcal{K}_+(\tau)A_+ + \mathcal{K}_-(\tau)A_- \\ A_+ &= (L_1 + L_2 + L_3)R(\tau)(L_1 + L_2 + L_3)R(-\tau) \\ A_- &= (L_1 + L_2 + L_3)R(\tau)(M_1 + M_2 + M_3)R(-\tau). \end{aligned} \quad (\text{C.5})$$

In this expression one can eliminate the terms which contain higher orders in the Planck constant  $\hbar$ . According to equation (C.2) the terms containing  $\hbar^n$  with  $n > 2$  vanish when taking the classical limit. The analysis of orders of magnitude in equation (C.5) follows from the estimate of such orders pertaining to its ingredients:

$$\begin{aligned} M_1 &\sim 1 \\ L_1, L_2, M_2 &\sim \hbar \\ L_3, M_3 &\sim \hbar^2. \end{aligned} \quad (\text{C.6})$$

The low order for  $M_1 = 2p_y$  looks unusual. It can be, however, shifted by invoking integration by parts as described in appendix D. So, we introduce the function

$$\Gamma(\tau) = \int_0^\tau d\tau' \mathcal{K}_-(\tau') \quad (\text{C.7})$$



in terms of which the following identity is obtained:

$$-\int_0^\infty \mathcal{K}_-(\tau) L_1 R(\tau) M_1 R(-\tau) d\tau = \int_0^\infty \Gamma(\tau) L_1 R(\tau) 2B(y) R(-\tau) d\tau \quad (\text{C.8})$$

where  $B(y)$  is the diagonal matrix defined in equation (5.8). From equations (4.10) we observe also that

$$\frac{2i}{\hbar} \Gamma(\tau) = \frac{1}{k_B T} K_+(\tau) \quad (\text{C.9})$$

in the classical limit ( $\frac{\hbar\omega}{k_B T} \gg 1$ ). By this means, the order of  $M_1$  is shifted higher by one point, according to equation (C.8).

### C.3. Simplifying assumptions

After utilizing equations (C.8) and (C.9) we can turn back to equation (C.5). With these precautions, the simplified expression for the relaxation operator is obtained by counting orders of magnitude of its ingredients, withdrawing higher-order terms and performing the substitution (C.5) in the remaining expression. Such an analysis separates the leading terms and provides the expression

$$\begin{aligned} A_+ &= L_1 R_0(\tau) L_1 R_0(-\tau) + L_2 R_0(\tau) L_2 R_0(-\tau) \\ A_- &= L_1 R_0(\tau) M_1 R_0(-\tau) + L_2 R_0(\tau) M_2 R_0(-\tau). \end{aligned} \quad (\text{C.10})$$

Three remaining nonvanishing terms (i.e. those having the order  $\hbar^2$ ) are excluded from equation (C.10):

$$\begin{aligned} &L_1 R_0(\tau) L_2 R_0(-\tau) \\ &L_2 R_0(\tau) L_1 R_0(-\tau) \\ &L_2 R_0(\tau) M_1 R_0(-\tau). \end{aligned} \quad (\text{C.11})$$

In equation (C.10) the first components (containing  $L_1$  and  $M_1$ ) generate diffusion terms; the second components (containing  $L_2$  and  $M_2$ ) are responsible for nonadiabatic transitions. The interference terms (C.11) are omitted in the further treatment.

Neglecting interference terms will be also complemented by neglecting the commutator  $[L_1, R_0]$  in equation (C.10). This commutator generates terms similar to (C.11). It vanishes exactly in the case when the energy difference  $\Delta(y) = \varepsilon_2(y) - \varepsilon_1(y)$  becomes constant (see figure 1(c)). Actually, the condition  $\frac{\partial \Delta}{\partial y} = 0$  is acceptable, because, in the adiabatic representation, the interlevel transitions are localized in the vicinity of extremum points of the adiabatic energy profiles.

## Appendix D. The integration by parts of the relaxation operator

Consider the expression

$$K_2 = -\frac{1}{\hbar^2} \int_0^\infty d\tau \mathcal{K}_-(\tau) L_1 R(\tau) A(y, p_y) R(-\tau). \quad (\text{D.1})$$

Here  $A$  represents a  $\tau$ -independent Liouville matrix including  $y$  and  $p_y$  which are considered as time-independent phase space variables. The following identity is valid:

$$\frac{d}{d\tau} [R(\tau) A R(-\tau)] = -\frac{i}{\hbar} R(\tau) [L[\hbar], A] R(-\tau) \quad (\text{D.2})$$

where  $[\dots, \dots]$  denotes a commutator of Liouville matrices. When performing integration by parts in equation (D.1) we need a notation

$$\Gamma(\tau) = \int_0^\tau d\tau \mathcal{K}_-(\tau) = \sum_v \gamma_v^2 \frac{\hbar}{2i} \cos \omega_v \tau. \quad (\text{D.3})$$

The result reads

$$K_2 = \int_0^\infty \left( -\frac{i}{\hbar} \Gamma(\tau) \right) d\tau \{L_1 R(\tau) [L[h], A] R(-\tau)\}. \quad (\text{D.4})$$

When  $A = M_1 = 2p_y$  one obtains from equation (5.6)

$$[L[h], 2p_y] = 2i\hbar B(y) \quad (\text{D.5})$$

thus giving rise to equation (C.8). In deriving equation (D.4) the following interpretation of equation (D.1) is required: we consider  $\mathcal{K}_-(\tau)$  as a causal function ( $\mathcal{K}_-(\tau) = 0$  for  $\tau < 0$ ) and extend the lower integration limit as  $\tau = -\infty$ .

Note that the similar transformation is valid when we change  $L_1$  in equation (D.1) for  $L_2$  or  $L_3$ . In the same way any terms in the second (anticommutator) part of equation (C.5) can be rearranged.

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