New mechanism for non-trivial intra-molecular vibrational dynamics.

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We investigate the time evolution process of one selected (initially prepared by optical pumping) vibrational molecular state \( S \), coupled to all other intra-molecular vibrational states \( R \) of the same molecule, and also to its environment \( Q \). Molecular states forming the first reservoir \( R \) are characterised by a discrete dense spectrum, whereas the environment reservoir \( Q \) states form a continuous spectrum. Assuming the equidistant reservoir \( R \) states we find the exact analytical solution of the quantum dynamic equations. \( S \) - \( Q \) and \( R \) - \( Q \) couplings yield to spontaneous decay of the \( S \) and \( R \) states, whereas \( S \) - \( R \) exchange leads to recurrence cycles and Loschmidt echo at frequencies of \( S \) - \( R \) transitions and double resonances at the interlevel reservoir \( R \) transitions. Due to these couplings the system \( S \) time evolution is not reduced to a simple exponential relaxation. We predict various regimes of the system \( S \) dynamics, ranging from exponential decay to irregular damped oscillations. Namely, we show that there are four possible dynamic regimes of the evolution: (i) - independent of the environment \( Q \) exponential decay suppressing backward \( R \) - \( S \) transitions, (ii) Loschmidt echo regime, (iii) - incoherent dynamics with multicomponent Loschmidt echo, when the system state exchanges its energy with many states of the reservoir, (iv) - cycle mixing regime, when the long term system dynamics appear to be random. We suggest applications of our results for interpretation of femtosecond vibration spectra of large molecules and nano-systems.

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I. INTRODUCTION

A quasi-stationary state in quantum mechanics occurs as a result of overlapping (superposition) of an initially localised (stationary) state with the states (i.e., wave functions) from continuous spectrum formed by either free states of the same system (separated from the initial state by a potential barrier, as in the case of \( \alpha \)-decay), or by the system environment (see classical papers [1], [2]). Following this, common wisdom ascribes irreversible evolution of quasi-stationary states by coupling the states to a reservoir with continuous spectrum [3], [4]. With a model reservoir formed by a sea of harmonic oscillators, this approach is at the heart of the theory of quantum dissipative systems [5], [6], [7].

An opposite limit is considered in the theory of transition states which is widely used to treat various chemical dynamics problems [8], [9]. In this microscopic approach one has to choose properly a set of internal degrees of freedom forming a so-called reaction path, and a small number of transverse degrees of freedom which are coupled to the longitudinal reaction coordinate. This microscopic description is feasible in practice up to a few dozens of the transversal degrees of freedom. For larger systems the microscopic approach becomes useless (since even with modern computer powers it is almost impossible to solve a system of dynamic equations with \( 10^4 \) transversal degrees of freedom for all eigen states to restore multidimensional potential energy surfaces). However many nano-systems with \( 10^2 - 10^4 \) degrees of freedom, interesting from their practical importance and the associated theoretical challenges, belong to an intermediate case when both of the above mentioned approaches (macroscopic theory of quantum dissipative systems and microscopic theory of chemical dynamics) do not work. Evidently to cover these very complex phenomena, it is necessary as a first step at least to choose an appropriate simple model. One approach is to borrow concepts from other physical systems with dense discrete spectra, for example nuclei. It was shown in [10], [11], [12], [13], [14], that statistical description of such systems does not require any detailed information about its spectrum, but only a few universal spectral characteristics (like interlevel spacing distribution function), determined by a random Hamiltonian matrix. This approach is a very convenient tool to describe spectral chaos and many other global features of the behavior, but it says almost nothing about quantum dynamics, in which we are interested in this paper. Our motivation is not a pure curiosity. As a matter of fact quantum dynamics of various systems (ranging from relatively
small molecules in a pre-dissociation condition \cite{15, 16} up to large photochromic molecules and protein complexes \cite{17, 18, 19, 20, 21, 22}, or molecules confined near interfaces \cite{23} (see also \cite{22}) is an active area of experimental research. Femtosecond spectroscopy data (which allows the study of the time evolution of one initially prepared by the optical pumping state) manifest a variety of possible dynamic regimes including not only weakly damped more or less regular oscillations but also very irregular long term behavior with a number of peaks corresponding to a partial recovery of the initial state population.

Seemingly irregular damped oscillation regimes observed in such systems cannot be explained theoretically in the frameworks of widely used models with reservoirs possessing continuous spectra \cite{24, 25, 26, 27}. Indeed in the case of a system coupled to the continuous spectrum reservoir, only a smooth crossover between coherent oscillations and an exponential decay is possible upon increasing of the coupling. Nevertheless, as it was shown in the papers cited above, generic complex dynamics is observed in the systems with characteristic inter-level spacing of the order of 10 cm$^{-1}$, when the measurements are performed in the range of sub-picoseconds, or femtoseconds. To explain these weakly damped oscillations semi-empirical models have been proposed \cite{22, 23}, assuming more or less arbitrarily that the system interacts not only with the environment (possessing continuous spectrum in the agreement with a common belief), but also with a few weakly damped discrete vibrational levels. However, these models providing a possible mechanism for weakly damped oscillations, do not explain irregular, random-like dynamic evolution. It is worth noting again that a generic feature of systems with such irregular behavior is the existence of the dense but discrete vibrational spectra, about $10^2 - 10^3$ levels, and characteristic inter-level spacing of the order of 10 cm$^{-1}$. This generic feature is present in all systems with complex and irregular vibrational relaxation. Motivated by these observations, our intent here is to propose a simple (but yet non-trivial) model of a system coupled to a reservoir with a discrete spectrum, and to examine joint system-reservoir evolution, i.e., recurrence cycles, when the energy is flowing back from the reservoir to the system, and to apply this model to intra-molecular vibrational relaxation.

Vibrational relaxation in large molecules is one of the most relevant processes in chemical dynamics. The system time evolution includes as its step intra-molecular energy transfer via transitions from a specially prepared and selected initial molecular state (system $S$) to a large finite number of distinct levels of the same molecules. This intra-molecular evolution should be supplemented, of course, by the interaction of all these states that possess a continuous spectrum environment, which ultimately yields to conventional exponential relaxation \cite{28}. To describe theoretically these radiationless transitions, usually one has to rely on approximate treatment of the system - reservoir interactions, e.g., on random phase approximation. In this case the system time evolution is determined by the decay rate constant, which is calculated accordingly with the famous Fermi Golden Rule. Unfortunately such an approach is valid only in the limit of a relatively weak system - reservoir coupling, when calculating perturbatively transition probability, one may neglect shift of the energy levels \cite{30}.

In our paper we develop another approach to analyse theoretically the problem of intra-molecular vibrational dynamics. Instead of a perturbative solution to the quantum dynamic equations for a system coupled to an arbitrary reservoir, we find the exact solution for a simple model of a reservoir spectrum (i.e., a set of final states). The model keeps the main essential feature of intra-molecular vibrational dynamics, namely that realistic reservoir should possess discrete and dense spectrum of its states. Surprisingly enough, scanning the literature we could not find any paper treating theoretically such a model. We do believe that the basic ideas inspiring our work can be applied to a large variety of interesting nano-systems. In the recent short publication \cite{31} such a model of a system coupled to a reservoir with dense discrete spectrum was proposed, and under assumptions put forward by Zwanzig \cite{32} (equidistant spectrum of the reservoir and system-reservoir coupling independent of reservoir state quantum numbers) its exact analytic solution was found. Here we generalise this approach to rationalise intra-molecular vibrational relaxation in terms of time evolution of quasi-stationary states. The key feature, indispensable to provide energy exchange between the system and reservoir, is backward energy flow, which is ignored in all models with continuous spectra of final states \cite{6}. These backward transitions (and corresponding recurrence cycles or Loschmidt echo phenomenon) are the main new physical ingredients of our approach, and they are responsible for non-trivial time evolution. For a fairly broad class of molecules, such a non-trivial time evolution indeed was observed experimentally (see the monographs in \cite{33, 34} and references therein) by modern femtosecond spectroscopy technique. Our model seems to be adequate to rationalise these experimental observations, in a sense that we are not aiming at the best quantitative agreement of theoretical results and experimental data but at the identification, understanding and explanation of important sources of non-exponential time evolution.
II. BASIC THEORETICAL NOTIONS FOR A MODEL WITH TWO RESERVOIRS.

Our analysis is based on a simple but very general observation known from standard quantum mechanics. For a selected unperturbed energy level $\epsilon_0^s$ (in what follows we will term the level as a system) coupled to a discrete spectrum reservoir (with its unperturbed energy states $\{\epsilon_n^r\}$), the Hamiltonian matrix contains besides the main diagonal, only one row and one line of non-zero matrix elements:

\[
\begin{pmatrix}
... & ... & ... & ... & ... & ... & ... \\
... & \epsilon_1 & 0 & 0 & C_1 & 0 & ...
\end{pmatrix}
\]

Therefore the corresponding secular equation (its roots determine the coupled system-reservoir eigenvalues) has the following deceptively simple form:

\[
F(\epsilon) = \epsilon - \sum_n \frac{C_n^2}{\epsilon - \epsilon_n^r} = 0,
\]

where we count the energy levels from $\epsilon_0^s$, and to get such a compact form for the function $F(\epsilon)$ we use the orthogonal basis of the reservoir states, i.e., all matrix elements between the reservoir states are zero. With the same approach we can include all ingredients of radiationless molecular transitions into a simple model, namely

- system $S$ which is selected molecular level
- discrete dense spectrum $\{\epsilon_n^r\}$ reservoir $R$, which includes all other than $S$ molecular states
- $S - R$ coupling characterized by the coupling matrix elements $\{C_n\}$
- second reservoir (environment) $Q$ with continuous spectrum, which leads to a decay of the system $S$ (with its rate constant $\Gamma_s$) and of the reservoir $R$ states (with corresponding constants $\{\Gamma_n\}$).

One can derive formally an exact secular equation similar to the $S$ for the system $S$ and reservoir $R$ eigenvalues, which additionally includes the environmental level broadening (due to $S - Q$, and $R - Q$ couplings). The corresponding determinant contains (besides the diagonal matrix elements $E + i\Gamma_s$, and $\{E - \epsilon_n^r + i\Gamma_n\}$) only one non-zero row and one line with non-zero $S - R$ coupling matrix elements. The corresponding secular equation reads as

\[
F(E) \equiv E + i\Gamma_s - \sum_n \frac{C_n^2}{E - \epsilon_n^r + i\Gamma_n} = 0.
\]

Of course for arbitrary functions $C_n$, $\epsilon_n^r$, and $\Gamma_n$, the sum in the Eq. (3) cannot be calculated analytically. To proceed further on we are following the Zwanzig idea [32] (already broadly used in the theory of radiationless transitions [26 - 29], and time resolved spectroscopy [31, 35, 36]) assuming that

\[
\epsilon_n^r = n; \quad C_n = C; \quad \Gamma_n = \Gamma,
\]

where as above, we count all energy levels from the system $S$ energy unperturbed by its coupling to the reservoir levels, and the unperturbed reservoir $R$ interlevel spacing is chosen as the energy unit. It is worth noting also that the approximation of equidistant $R$ reservoir spectrum is not a completely artificial one. Indeed, for any system with a sufficiently large finite number of degrees of freedom, mutual level repulsion unavoidably favours to more or less equidistant interlevel spacing. A more realistic model will not affect our qualitative conclusions, and transparency is worth a few simplifications. If the Zwanzig model assumptions are granted, the secular equation (4) can be written in the following compact and easily solvable form

\[
F(E) = E + i\Gamma_s - \pi C^2 \cot[\pi(E + i\Gamma)] = 0.
\]
System $S$ and reservoir $R$ energy states can be regarded as quasi-stationary ones if
\[ \Gamma_s \ll 1; \Gamma \ll 1, \quad (6) \]
then complex solutions to the secular equation (5) are
\[ E_n = \epsilon_n - i\gamma_n, \quad (7) \]
where
\[ \epsilon_n = \pi C^2 \cot(\pi \epsilon_n) + (\Gamma_s - \Gamma)^2 \left[ \epsilon_n \cot(\pi \epsilon_n) + \pi C^2 \right] \cot(\pi \epsilon_n) + \frac{1}{\pi}, \quad (8) \]
and
\[ \gamma_n = \Gamma + (\Gamma_s - \Gamma) \frac{1}{\epsilon_n \cot(\pi \epsilon_n) + \pi C^2 + (1/\pi)}. \quad (9) \]
Note that the shift of the zero level energy corresponds to a change of variables in a rotating frame, and it does not affect system dynamics in which we are interested in this work. By a simple inspection of the Eqs. (8) - (9) we conclude that $S-Q$ and $R-Q$ couplings displace the system $S$ and reservoir $R$ levels into the lower complex semiplane with energy dependent decay rates. $S-Q$, $R-Q$, and $S-R$ interactions yield to variations of all energy levels. It is easy to see that the energy level shifts $"\epsilon_n - n"$ are mainly due to $S-R$ coupling. It means that independent of the coupling strength $C$ there is one energy level in each interval $[n, n+1]$.

### III. SYSTEM AMPLITUDE

To analyse the system time evolution we have to solve the time dependent equations of motion (i.e., the corresponding Heisenberg equations of motion) for the system state amplitude $a_s$. Our Hamiltonian model describing the system $S$ and the discrete spectrum reservoir $R$ (while producing decay of the quasi-stationary states couplings with the continuous spectrum reservoir $Q$ are taking into account by introducing the decay rates $\Gamma_s$ and $\Gamma_n$ into the equations)
\[ H = \epsilon_s b_s^+ b_s + \sum_n \epsilon_n b_n^+ b_n + \sum_n C_n (b_s^+ b_n + b_s b_n^+), \quad (10) \]
where $b_s^+$, $b_n^+$ are corresponding creation operators. Time dependent wave functions $\Psi_s(t)$ of the Hamiltonian can be expanded over the unperturbed (uncoupled) eigenfunctions of the system $\Phi_s$ and of the reservoir states $\Phi_n$
\[ \Psi_s(t) = a_s(t) \Phi_s + \sum_n a_n(t) \Phi_n \quad (11) \]
with time dependent amplitudes $a_s(t)$, $a_n(t)$. These time dependent amplitudes satisfy the corresponding Heisenberg equations of motion. Combining everything together we end up with a general case (i.e., not applying immediately the Zwanzig approximation), the equations read (in units with $\hbar = 1$, and dots steam for time derivatives)
\[ i \dot{a}_s = -i\Gamma_s a_s + \sum_n C_n a_n; \quad i \dot{a}_n = (\epsilon_n - i\Gamma_n) a_n + C_n a_s. \quad (12) \]
The solution to the Eq. (12) supplemented by the initial conditions
\[ a_s(0) = 1; a_n(0) = 0, \quad (13) \]
can be formally found as
\[ a_s(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \exp(-iEt) \left( E + i\Gamma_s - \sum_n C_n^2 \left( E + i\Gamma_n - \epsilon_n \right) \right)^{-1}. \quad (14) \]
The amplitude can also be expressed as a sum of residues in the poles of the integrand in the Eq. (14) which are the roots of the secular equation (3)

\[ a_s(t) = \sum_n \exp(-iE_n t) \left| \frac{dF}{dE} \right|_{F(E) = 0} . \] (15)

Let us apply now the Zwanzig approximation (4). In this case the formal solution for the system amplitude (15) can be written down in the explicit analytical form

\[ a_s(t) = \sum_{n=-\infty}^{n=\infty} \frac{\exp(-iE_n t)}{1 + \pi^2C^2 + C^{-2}(E_n + i\Gamma_s)^2} = 2 \sum_{n=0}^{n=\infty} \exp(-\gamma_n t)[B_n \cos(\epsilon_n t) + S_n \sin(\epsilon_n t)] , \] (16)

where

\[ B_n = B[\epsilon_n^2 - (\Gamma_s - \gamma_n)^2 + C^2(1 + \pi^2C)^2] ; \] (17)

and

\[ S_n = 2B\epsilon_n(\Gamma_s - \gamma_n) . \] (18)

The coefficients in these formulas reads as

\[ B = C^2[(\epsilon_n^2 - (\Gamma_s - \gamma_n)^2 + C^2(1 + \pi^2C)^2) + 4\epsilon_n^2(\Gamma_s - \gamma_n)^2]^{-1} . \] (19)

The above expressions (19) - (19) give the exact solution to describe quantum dynamics of the system S coupled to the Zwanzig reservoir R and continuous spectrum environment reservoir Q.

IV. RECURRENCE CYCLE AMPLITUDE REPRESENTATION

Presented in the previous section exact results are not very useful in practical terms, because of a poor convergence of Fourier series entering these expressions. Luckily one can transform the results into a form more convenient for further calculations (both analytical and numerical) by replacing the Fourier expansion with the expansion over partial recurrence cycle amplitudes. The method of how to do it, developed in the papers [31, 39, 35], is based on the Poisson summation formula, (see e.g., [40]). To transform \( a_s(t) \) as it is given in the (16), we introduce the following formal identity for the \( \delta \) function

\[ \delta(E(x)) = \sum_n \left| \frac{dE}{dx} \right|^{-1} \delta(x - n) . \] (20)

The Eq. (20) allows us to replace the discrete variables \( n \) and \( E_n \) by their continuous counterparts \( x \) and \( E(x) \) with \( E(n) \equiv E_n \). Thus we end up with

\[ a_s(t) = \sum_n \left( \frac{dF}{dx} \right)^{-1} \exp(-iEt)\delta(E - E_n) = \sum_{k=-\infty}^{\infty} \int_{-\infty}^{\infty} dE \left( \frac{dF}{dE} \right)^{-1} \left( \frac{dE}{dx} \right)^{-1} \exp[-iE(t - 2k\pi) + i2k\pi(E - x)] . \] (21)

The expression (21) represents system evolution as a sum over recurrence cycles

\[ a_s(t) = \sum_{k=-\infty}^{\infty} a_s^{(k)}(t - 2k\pi) , \] (22)

where the partial cycle \( k \) amplitude (for Zwanzig reservoir R) reads as

\[ a_s^{(k)}(t - 2k\pi) = C^2 \exp(-2k\pi\Gamma) \int_{-\infty}^{\infty} dE \frac{(E + i\Gamma_s - i\pi C^2)^k}{(E + i\Gamma_s + i\pi C^2)^{k+1}} \exp[-iE(t - 2k\pi)] . \] (23)
In the initial cycle $k = 0$, there are two poles $E_{+-}^k = -i(\Gamma_s \pm \pi C^2)$ in the integrand for $a^{(0)}_s$, and for $t > 0$ only the pole $E_{+}^k$ contributes, yielding to the exponential relaxation law for the $a^{(0)}_s(t)$

$$a^{(0)}_s(t) = \exp[-(\Gamma_s + \pi C^2)].$$

We see that $S - R$ coupling gives an additional (with respect to the environment $Q$) decay channel with its rate

$$\Gamma_R = \pi C^2.$$

In a higher order recurrence cycles $k \geq 1$, the pole $E_{+}^k$ disappears and the residue in the $(k + 1)$-th order pole $E_{+}^k$ leads to

$$a^{(k)}_s(t - 2k\pi) = \exp[-2k\pi \Gamma] \exp[-\Gamma_s(t - 2k\pi)]a^{(k)}_{s0},$$

where for the sake of compactness

$$a^{(k)}_{s0}(t) = -\frac{2\Gamma_R(t - 2k\pi)}{k}L^1_{k-1}[2\Gamma_R(t - 2k\pi)]\Theta(t - 2k\pi).$$

Here $k \geq 1$, $L^1_{k-1}$ is adjoint Laguerre polynomial [41], and $\Theta(z)$ is a step function defined as $\Theta(z < 0) = 0$, and $\Theta(z > 0) = 1$. Since the pole $E_{+}^k$ exists only for $t \geq 2k\pi$ in the representation of the recurrence cycle partial amplitudes for $a_s(t)$ only the cycles with $k$ ranging from 0 to $[t/2\pi]$ ($[x]$ stands for the integer part of $x$) contribute into the sum entering equations (21) - (22).

Similarly the amplitudes for the reservoir $R$ states can be written as

$$a_n(t) = \sum_{k=0}^{[t/2\pi]} a^{(k)}_n(t - 2k\pi),$$

where for $k = 0$

$$a^{(0)}_n(t) = \frac{C}{n + i(\Gamma_s + \Gamma_R - \Gamma)}(\exp[-(\Gamma_s + \Gamma_R)t] - \exp[-(in + \Gamma)t]),$$

and for $k \geq 1$

$$a^{(k)}_n(t - 2k\pi) = -iC \exp[-(in + \Gamma)(t - 2k\pi)] \int_0^{(t - 2k\pi)} dt' \exp((in + \Gamma)t')a^{(k)}_n(t').$$

It is worth noting that although transformation from the Fourier representation into the partial amplitude representation mathematically is merely a change of variables, there is some physics behind it. By inspection of both representations one can see that the Fourier expansion coefficients are determined by the real eigenvalues, while the partial amplitudes depend mainly on imaginary pole displacements (which in their own turn are related to the $S - R$ coupling or decay rate $\Gamma_R$). This is not a minor technical issue but an essential physical difference, because in fact it means that the partial recurrence cycle amplitudes take into account effects of all $R$ states. Physics occurs as a result of it. Indeed quantum interference of transitions from different $R$ states suppresses effectively back transitions from the $R$ states into the system $S$, and yields to a new decay channel. Its decay rate is determined by the transition probability into all $R$ states. Back transitions from the $R$ states into the system lead also to the spontaneous Loschmidt echo at each recurrence cycle. Instead of an individual level-to-level transition picture (satisfying standard detailed balance relations) we have to deal with cooperative transitions from $S$ into all $R$ states. $\Gamma_R$ is the rate of these transitions, and for the backward transitions from $R$ to $S$ the effective rate constant is of the order of unity, because the reservoir $R$ should ”wait” for synchronisation of its states to have backward $R$ to $S$ transition.

This non-trivial behavior manifests itself in a fine structure of the Loschmidt echo signals. Utilising known properties of the Laguerre polynomials [41] we arrive at the conclusion similar to that found in [31], [39], [35] for a single reservoir Zwanzig model. Namely, that in the $k$-th recurrence cycle, the Loschmidt echo signal has $k$ components, $I_{kk}$ with $l = 1, \ldots, k$. The component $I_{kk}$ is the most intense one. Because different $R$ states exchange their populations with the system $S$ not at the same time, the echo signal is broadened. The full width of the signal in the cycle $k$ is about $4k$. In its own turn when $k$ grows, the Loschmidt echo signals for the neighboring cycles start to overlap, if $k > k_c = \pi^2 C^2$, and for $k \gg k_c$ time evolution looks as irregular (quasi-stochastic) damped oscillations.
It is also interesting to compare the formally exact presentation of $a_s(t)$ in terms of the partial cycle amplitudes $a_k^s$ with its approximate treatment according to the Golden Fermi Rule. The equations of motion (12) written in the equivalent integral form can be rewritten as the quantum Langevin equation for kicked harmonic oscillations with friction

$$\dot{a}_s(t) = -\Gamma_s a_s - \int_0^t dt' a_s(t') \sum_n C_n^2 \exp[-i(\epsilon_n^0 - i\Gamma_n)(t-t')].$$

(31)

The terms entering this equation have transparent physical meaning: the resonance transition to the level $n = 0$ of the reservoir leads to coherent oscillations with frequency $\propto C$, whereas non-resonance ($n \neq 0$) transitions produce effective friction and exciting force. However, strictly speaking, there is no stochasticity in the equation, and we have fully deterministic energy levels and therefore time evolution.

In the Golden Fermi Rule approximation we replace

$$\sum_n \rightarrow \int_{-\infty}^{\infty} \rho(\epsilon) d\epsilon,$$

(32)

with $\rho(\epsilon)$ being unperturbed (by interactions) density of states. Furthermore, if $C_n^2(\epsilon_n^0)\rho(\epsilon_0)$ is a slow varying (in comparison to exponential) function, the integrand in the (31) - (32) can be approximated by the mean value of this function. Thus, according to the Golden Fermi Rule

$$\dot{a}_s(t) = - (\Gamma_s + \Gamma_{GFR}),$$

(33)

where $\Gamma_{GFR} = 2\pi \langle C^2(\epsilon)\rho(\epsilon) \rangle$, and therefore in this approximation the memory about all recurrence cycles is lost. For a single reservoir Zwanzig model this approximation corresponds to keeping only one term $k = 0$ in the Poisson summation formula.

V. TIME EVOLUTION REGIMES

The partial cycle amplitudes $a_k^s$ are represented according to the expressions (26), (27) as a product of three factors. The first factor is related to the $R - Q$ coupling. Physically it describes the Loschmidt echo signal reduction due to spontaneous decay of the $R$ states in the previous (with respect to the cycle $k$ under consideration) cycles. In the strong coupling limit we are interested in, i.e., for $\Gamma_R \gg 1$, this factor does not depend on $\Gamma_s$. Indeed in this limit in the major part of the recurrence cycle only the reservoir $R$ states are populated, whereas the system population is negligibly small. The second factor in the Eqs. (26), (27) is related to the system decay in the same cycle $k$. Naturally this factor does not depend on the decay rate of the reservoir $R$ states. Finally the third factor in the (26), (27) is related to the decay rate the system at $\Gamma_s = \Gamma = 0$.

These relations (26) - (27) and their interpretation are our main results in this paper. Analysing the relations we end up with the following classification of the possible time evolution regimes. Namely

- Exponential decay in the initial cycle $k = 0$, when the Loschmidt echo intensity is exponentially small

$$\Gamma \gg \frac{1}{2\pi}.$$

(34)

If $\Gamma_R \gg \Gamma_s$ then the decay rate $\Gamma_R + \Gamma_s \simeq \Gamma_R$ does not depend on the reservoir $Q$. Physically it means that in this limit the rate of radiationless intra-molecular transitions is independent of the molecular environment $Q$. The states of the $R$ reservoir with $|n| \leq \Gamma_R$ gives the main contributions into the $S$ state decay rate (dominated in this limit by the $S-R$ exchange). These reservoir states populations monotonously increase at $\Gamma_R t \leq 1$ and achieve maximal values at $T^* \simeq \Gamma_R^{-1} \ln(\Gamma_R/\Gamma)$. Then the state $n$ population decreases as

$$|a_n(t)|^2 = \frac{\Gamma R}{\pi(n^2 + (\Gamma_R + \gamma_s - \Gamma)^2)} (\exp(-\Gamma t) - \exp(-(\Gamma_R + \Gamma_s) t)).$$

(35)
• Regular Loschmidt echo regime, where stochastic-like behavior is not achievable, because the echo intensity is already negligibly small when the cycles start to mix

\[ \frac{1}{2\pi} > \Gamma > \frac{1}{2\pi k_c}; \Gamma_R \geq 1 > \Gamma_s. \] 

(36)

In this regime we get Loschmidt echo phenomenon which occurs due to synchronisation of the backward (from the reservoir \( R \) into the system \( S \)) transitions. Furthermore when the state \( n \) of the reservoir is de-populated completely, its complex amplitude \( a_n(t) \) acquires the phase shift \( \pi \). This leads to resonance behavior at the double reservoir \( R \) interlevel transition frequency. In turn these double transitions \( n \rightarrow s \rightarrow n' \) effectively redistribute the population between the reservoir \( R \) states. Besides the phase shift \( \pi \) yields to \( a_n(t) \) sign alternation between even and odd cycle numbers (see the Fig. 1). In odd cycle numbers the energy (or population) flows from the reservoir \( R \) into the system, whereas in even cycle numbers it flows from the system into the reservoir states.

• Quasi-stochastic time evolution when

\[ \frac{1}{2\pi} > \Gamma > \frac{1}{2\pi k_c}; 1 > \Gamma_R > \Gamma_s, \] 

(37)

when the system time evolution is described by incoherent dynamics with multicomponent Loschmidt echo. In this case the system exchanges its energy with many states of the reservoir.

• Cycle mixing regime

\[ \Gamma \ll \frac{1}{2\pi k_c}; \Gamma_R \gg 1 \gg \Gamma_s. \] 

(38)

In this case the cycles are strongly overlapped, the system amplitude oscillates in a shorter and shorter time scale, because the number of zeros of the \( a_s(t)^{(k)} \) in the cycle \( k \) increases proportionally with \( k \). Therefore to keep fully deterministic system description at \( t \rightarrow \infty \), one has to know the system evolution at shorter and shorter time intervals. This phenomenon leads to effective loss of deterministic dynamics at arbitrary small time coarse-graining, related physically to uncertainties of the system or of the reservoir, for example.

We see from these conditions that the Loschmidt echo occurs depending mainly on the decay rate of the \( R \) states, whereas stochastic like behavior occurs depending on the product of \( \Gamma \cdot \Gamma_R \), which characterises the energy (or level population) flow from the system into the environment \( Q \) through the reservoir \( R \) states as intermediate ones. We illustrate these findings in the Fig. 1 which shows how system level \( \epsilon_s \) population \((\propto |a_s(t)|^2)\) depends on the coupling to the reservoir \( R \) states. The \( S - Q \) coupling affects also the shape of the Loschmidt echo signal, suppressing upon

Figure 1: System population time evolution for the model parameters: \( C^2 = 1, \Gamma_s = 0.2 \). \( \Gamma \) shows how strong intramolecular vibrations are coupled to environment: (a) \( \Gamma = 0.01 \); (b) \( \Gamma = 0.05 \); (c) \( \Gamma = 0.15 \). Time is measured in the recurrence cycle period units \( 2\pi/\Omega \), where \( \Omega \) is the interlevel spacing in the reservoir \( R \).

\( \Gamma_s \) growing the most intensive echo component \( I_{kk} \). Our results demonstrate the main advantage of the partial cycle amplitude representation in comparison with the standard Fourier representation for the \( a_s(t) \) evolution. The latter one depends on the complex manner of interplay of all three relevant coupling parameters \( S - Q, R - Q, \) and \( S - R \), whereas in the former one these three interactions are factorised.
A. Averaged over cycle population of state

The system $S$ population averaged over a cycle $k$ is determined naturally as

$$
\langle |a_s^{(k)}|^2 \rangle_k \equiv \int_0^{2\pi} dt' |a_s^{(k)}(t')|^2.
$$

(39)

For non-overlapping cycles the upper integration limit in the (39) can be moved to infinity (since the integrand is exponentially small for $t' > 2\pi$). Replacing $a_s^{(k)}(t')$ in the (39) by its Laguerre polynomial explicit form (27), and utilising known [41] integrals with Laguerre polynomials we find

$$
\langle |a_s^{(k)}|^2 \rangle_k \simeq \Gamma^{-1}_R \exp(-4\pi \Gamma)(1 + \zeta)^{-3} \frac{F(-k+1,3/2,-k+3/2,(1-\zeta)/(1+\zeta))^3}{F(-k+1,3/2,-k+3/2,1)},
$$

(40)

where $F(a, b, c, z)$ is a hyper-geometric function [41], and $\zeta \equiv \Gamma_s / \Gamma_R$. When $\zeta \ll 1$, the (40) becomes $\zeta$-independent, and the averaged over cycle system state population decays with the $R - Q$ transitions rate constant $4\pi \Gamma$. Let us stress again the message we got from the comparison of the expression (24) for the initial cycle decay rate and the expression (40) for long-time evolution: the former is determined by the $S - Q$ transitions, whereas the latter one by the $R - Q$ transitions.

B. Notes on the coarse grained spectrum

As it was pointed out above, when $k$ (cycle number) is growing, the number of the fine structure components of the Loschmidt echo signals grows proportionally to $k$. As a result of increasing $k$, the echo shape becomes more and more complex. To detect the Loschmidt echo signal accurately one has to use a detector with better and better resolution because the signal shape upon $k$ growing includes more and more components. The same can be formulated that for a given detector resolution, there is always a certain cycle number, when the accuracy of the detector is not sufficient to resolve the Loschmidt echo signal. Therefore the finite accuracy of any detector device yields to the fact that one may not restore the energy spectrum by measuring the time evolution of the system amplitudes $a_s(t)$. Although mathematically speaking to restore the spectrum it is enough to perform inverse Fourier transform of the amplitude, in practical terms it is not possible, since the amplitude cannot be measured with the required accuracy for high enough cycle number. With a finite detector resolution we are able to perform only truncated Fourier transformation up to a certain limiting recurrence cycle number threshold $K_m$. We illustrate this message on a reduced accuracy of truncated Fourier transformation in the Fig. 2. Note that noise from the measurement device also restricts a spectrum part which can be reproduced from asymptotic behavior of $a_s(t)$. The Fig. 2c shows spectrum distortion induced by external white noise. Namely, we have calculated the $R$-reservoir absorption spectrum for the truncated at $K_m$

![Figure 2: Adsorption spectrum for the reservoir $R$ calculated by truncated Fourier transformation of the amplitudes for the model parameters $\Gamma = \Gamma_s = 0.1, C^2 = 1$, and the limiting by measurement precision recurrence cycle number $K_m$ is: (a) $K_m = 1$; (b) $K_m = 5$; (c) $K_m = 20$. In the Fig. 2c white noise produced by a measurement device (signal/noise ratio 10/1) is also added.](image-url)
small) no traces from the recurrence cycles are visible, and we get Fermi Golden Rule exponential decay. For the larger values of the $K_m$ (Fig. 2b) there are clear indications for adsorption peaks corresponding to the Loschmidt echo signals in $a_s(t)$. However, adding external white noise (Fig. 2c) we see that the adsorption peaks are reduced even for the bigger (than in the Fig. 2b) values of $K_m$. In its spirit the described mechanism is in the heart of quantum mechanical uncertainty produced by the interaction between quantum system and classical measurement device. It is considered as a route to quantum chaos and irreversibility phenomena [12], [3].

VI. CONCLUSION

To summarise, in this paper we investigated quantum dynamics of a single selected state of a small system. This selected state is coupled to other discrete dense states of the same system, and all the states are coupled also to continuous spectrum environment. This publication represents a substantial extension of the note [31], where only a single equidistant reservoir and constant-coupling Zwanzig model have been studied. Here we provide a more complete account and investigation of phenomena only briefly addressed in [31], and generalise the Zwanzig model to include quasi-stationary states and coupling to the second continuous spectrum reservoir - environment $Q$. We show that there are possible four dynamic regimes of the evolution:

- (i) - independent of the environment $Q$ exponential decay suppressing backward $R$ - $S$ transitions
- (ii) Loschmidt echo phenomenon occurring not only due to almost coherent oscillations governed by transitions from the system to the resonance reservoir $R$ state, but also due to double transitions $n \rightarrow s \rightarrow n'$ at the double reservoir $R$ interlevel transition frequency
- (iii) - incoherent dynamics with multicomponent Loschmidt echo, when the system is exchanged its energy with many states of the reservoir
- (iv) - cycle mixing regime, when due to unavoidable coarse graining in any real system of time or energy measurements, or initial condition uncertainty, the system loses invariance with respect to time inversion. In such conditions dynamic evolution of the system cannot be determined uniquely from the spectrum, and in this sense long term system dynamics appear to be random.

The quantum dynamics of the selected level demonstrates non-trivial fine structures of the recurrence cycles (Loschmidt echo) and cycle mixing leading eventually to irregular, chaotic-like long term evolution. Our results illustrate non-ergodic dynamics of such a system, i.e., system population (or its energy) is not equally distributed over all system states but in certain time intervals it is concentrated in a few levels. The generalised Zwanzig model investigated in this paper reflects the spirit of minimalist approaches, in that it is simple yet based on a physical principle. The results presented here are probably less notable in terms of technological applications of nano-systems, than for the progress they could generate in our understanding of their complicated vibrational spectra.

Our consideration yields quite reasonable qualitative description of a variety of vibrational relaxation regimes and mode selectivity observed in experiments, and the model under investigation appears to be the simplest one demonstrating that relatively small variation of the coupling enables us to change qualitatively the dynamic behavior. One of the main difficulties in a quantitative comparison of the results of our simplified model with specific experimental measurements or elaborated numerical simulations is the availability of an accurate connection between experimental control parameters and entering theoretical model coefficients. In this sense our model should be treated as a working hypothesis. Although it provides a qualitative insight to the intra-molecular vibrational dynamics, we are left with many questions unanswered which must be perused in further work. Understanding all its limitations, we nevertheless hope that our theory captures the essential elements of intra-molecular vibrational relaxation in nano-systems. Note that modern femtosecond spectroscopy methods (see e.g., [17] - [23], [43] - [44]) indeed demonstrate (in a qualitative agreement with our consideration) remarkably different types of behaviors (exponential decay and irregular damped oscillations) of relatively close in energy initially excited states. We believe that we are the first to explicitly address this issue.
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[1] W.F.Weiskopf, E.P.Wigner, Z.Phys., 63, 54 (1930).
[2] A.J.F.Siegert, Phys. Rev., 56, 750 (1939).
[3] P.Grigolini, Quantum Mechanical Irreversibility, World Scientific, Singapore (1993).
[4] I.Prigogin, T.Y.Petrovsky, Adv. Chem. Phys., 99, 1 (1997).
[5] A.J.Leggett, S.Chakravarty, A.T.Dorsey, M.P.A.Fisher, A.Garg, M.Zweber, Rev. Mod. Phys., 59, 1 (1987).
[6] U.Weiss, Quantum dissipative systems, World Scientific, Singapore (1999).
[7] L.H. Yu, C-P.Sun, Phys. Rev. A, 49, 592 (1994).
[8] V.A.Benderskii, D.E.Makarov, C.A.Wight, Chemical Dynamics at Low Temperatures, Willey-Interscience, New York (1994).
[9] V.A.Benderskii, E.V.Vetoshkin, I.S.Irgibaeva, H.P.Trommsdorff, Chem. Phys., 262, 369 (2000); ibid, 393.
[10] G.V.Milnikov, H.Nakamura, Phys. Chem. Chem. Phys., 10, 1374 (2008).
[11] O.Bohigas, S.Tomsovic, D.Ulmo, Phys. Rep., 223, 43 (1993).
[12] V.K.B. Kota, Phys. Rep., 347, 223 (2001).
[13] T.Papenbrock, H.A.Weidenmuller, Rev. Mod. Phys., 79, 997 (2007).
[14] M.L.Mehta, Random matrices, Academic Press, New York (1968).
[15] E.B.Stechel, E.J.Heller, Ann. Rev. Phys. Chem., 35, 563 (1984).
[16] L.H. Yu, C-P.Sun, Phys. Rev. A, 49, 592 (1994).
[17] V.A.Benderskii, K.B.Eisental, J. Phys. Chem., A, 106, 7482 (2002).
[18] M.Ben-Nun, T.J.Martinez, Chem. Phys. Lett., 298, 57 (1998).
[19] M.L.Mehta, Random matrices, Academic Press, New York (1968).
[20] M.Bixon, J.Jortner, J.Chem. Phys., 48, 715 (1968).
[21] P.Avouris, W.M.Gelbart, M.A.El-Sayed, Chem. Rev., 77, 973 (1977).
[22] K.Freed, A.Nitzan, J.Chem. Phys., 73, 4765 (1980).
[23] T.User, W.H.Miller, Phys. Repts., 199, 73 (1991).
[24] L. van Hove, Physica, 21, 901 (1955); 22, 343 (1956).
[25] V.A.Benderskii, L.A.Falkovsky, E.I.Kats, JETP Lett., 86, 311 (2007).
[26] R.Zwanzig, Lectures in Theor. Phys., 3, 106 (1960).
[27] A.H.Zewail, Femtochemistry: Ultrafast Dynamics of Chemical Bonds, World Scientific, Singapore (1994).
[28] S.Takahashi (Ed.), Time-resolved Vibrational Spectroscopy, Springer, Berlin (1992).
[29] Ya.B. Zeldovich, JETP, 12, 542 (1961).
[30] V.A.Benderskii, E.I.Kats, JETP Lett., 88, 338 (2008).
[31] P.Morse, H.Feshbach, Methods of Theoretical Physics, McGraw-Hill, New York (1953).
[32] H.Bateman, A.Erdelyi, Higher Transcendental Functions, v. 2, McGraw Hill, New York (1953).
[33] W.H.Zurek, Phys. Rev. D, 26, 1862 (1982).
[34] G.K.Paramonov, H.Naundorf, O.Kuhn, Eur. Phys. J. D, 14, 205 (2001).
[35] T.Schrader, A.Sieg, F.Koller, W.Schreier, Q.An, W.Zinth, P.Gielch, Chem. Phys. Lett., 392, 358 (2004).