

NON-TRIVIAL DYNAMIC REGIMES OF SMALL (NANO-SCALE) QUANTUM SYSTEMS

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Abstract. Small (but still containing many, about 10^2 – 10^4 , atoms) quantum systems (traditionally termed nano-systems) are dramatically different from their macroscopic or genuine microscopic (atomic) cousins. Microscopic molecular systems (with a few atoms) obey a regular quantum dynamics (described by time dependent Schrödinger equation), whereas in macroscopic systems with continuous energy spectra, one can expect regular dynamic behavior. The topic of our paper is in-between these limits. Nano-scale systems are characterized by small (but finite) mean interlevel spacing. In such a case with recurrence periods in picosecond range, Loschmidt echo and double resonance phenomena come into the game. System behavior becomes non-trivial and manifests a sort of transitions between regular and chaotic dynamics. We show that such dynamic transitions occur when the Loschmidt echo lifetime exceeds the typical recurrence cycle period. We illustrate this behavior in the framework of a few versions of the exactly solvable quantum problem, proposed long ago by Zwanzig [1]. It is based on the study of time evolution of the initially prepared vibrational state coupled to a reservoir with a dense spectrum of its vibrational states. In the simplest version of the Zwanzig model, the reservoir has an equidistant spectrum, and the system reservoir coupling matrix elements are independent of the reservoir states. We generalize the model to include into consideration the coupling of the initially prepared single state to system phonon excitations. The coupling re-

sults in the temperature dependent broadening and decay of the echo components. Another generalization is to replace a single level by two states coupled to the Zwanzig reservoir. We anticipate that the basic ideas inspiring our work can be applied to a large variety of interesting for the applications nano-systems (e. g., dissipative free propagation of excitations along molecular chains, or as a model for exchange reactions).

Introduction. There are materials which do not exhibit unusual properties in the nano-scale regime. For example, simple non-polar hydrocarbon molecules when aggregated are added merely additively. In other systems, that are under investigation in this work, the properties may exhibit anomalous values (or behavior of a system is unusual) in the nano-regime. Common wisdom borrowed from textbooks on quantum mechanics teaches that a population of somehow initially prepared state of a macroscopic system monotonically decreases in time due to the energy flow from this initial state into the states of the reservoir (formed by all continuous states of the macroscopic system under consideration). In the opposite limit (a small system with a few degrees of freedom), system behavior is also well known. The system dynamics is reduced to the recurrence cycles, with their periods (according to the famous Poincare theorem) determined by the lowest rationally independent interlevel spacings. As it is often the case, an intermediate case (relatively large but not macroscopically large quantum system) is the most difficult one for theoretical analysis. However, just such systems (generically termed as nano-systems) containing about several hundreds of atoms become more and more attractive for various applications.

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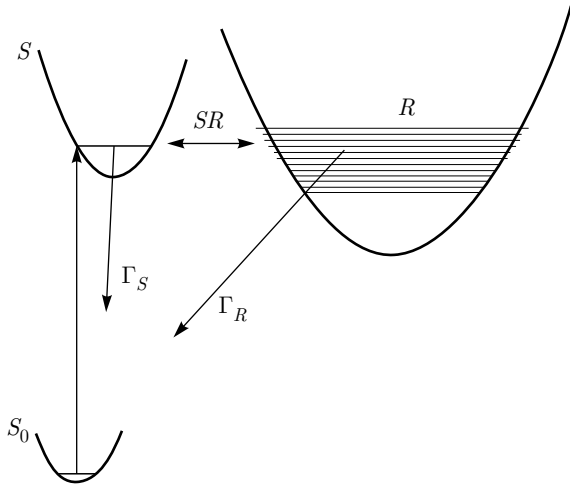


Fig. 1. Scheme of radiationless transitions $\{R_n\} \leftarrow S$ accompanying by the optical transition $S \leftarrow S_0$ from the ground to initial state. Direct optical transitions $\{R_n\} \leftarrow S_0$ are forbidden. S is the state obtained by the optical pumping from the ground state S_0 , $\{R_n\}$ are the final (reservoir) states, and Γ_S and Γ_R are decay rates for the corresponding states

Our intent in this work is to investigate dynamic behavior of these intermediate nano-size quantum systems. In principle, the full information about the system (both dynamics and statics) is naturally contained in quantum mechanical solution of the corresponding Schrödinger equation. In practice, however, the quantum solution is unfeasible even for not too large (about 10^2 – 10^4 atoms) systems. Therefore, one has to rely either on heavy *ab initio* numeric, or to look for analytically doable approximations. Luckily for us, many years ago Robert Zwanzig in a remarkable work (although published not in a regular and easy accessible journal [1]) proposed a simple (but not trivial) exactly solvable model of quantum dynamics. Within this model, an initially prepared single state of a quantum system evenly couples to the dense but discrete spectrum of the reservoir levels. Within the Zwanzig model, the coupling strength is assumed to be a constant independent of the reservoir levels. Surprisingly enough that in spite of this evidently erroneous assumption, Zwanzig approximation correctly identifies the dynamic regimes and characteristic time scales in the problem. Thus, although the Zwanzig model is a toy model (in the sense of caricaturing some physical features), when properly interpreted it can yield quite reasonable values for a variety of essential (and principally measured) quantities. That such a simple theory can predict rather complex and subtle features for nano-size quantum systems is remarkable.

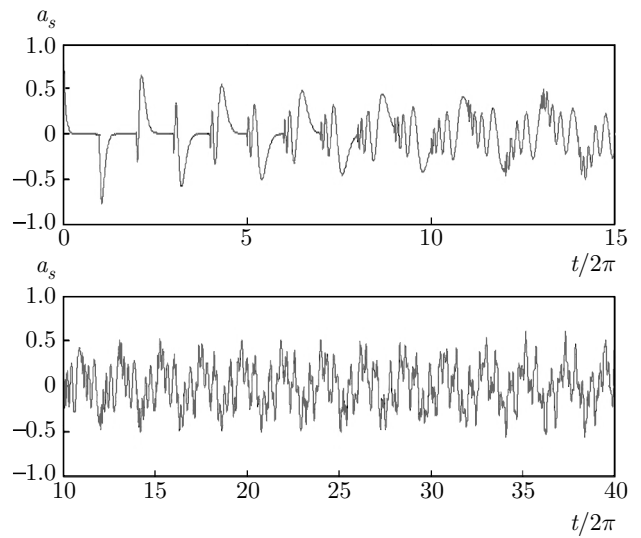


Fig. 2. The initial state evolution for the bare Zwanzig model: a_s is the amplitude of the optically excited state, C is the SR coupling constant, $C^2 = 1$, γ_s and γ_n are the widths of the corresponding energy levels (in the figure, the both $\gamma = 0$). Time is measured in the inverse interlevel spacing of the reservoir states. The upper panel shows the initial cycles with the regular dynamics. The lower panel demonstrates chaotic-like long-time dynamics in the case of the overlapping recurrence cycles

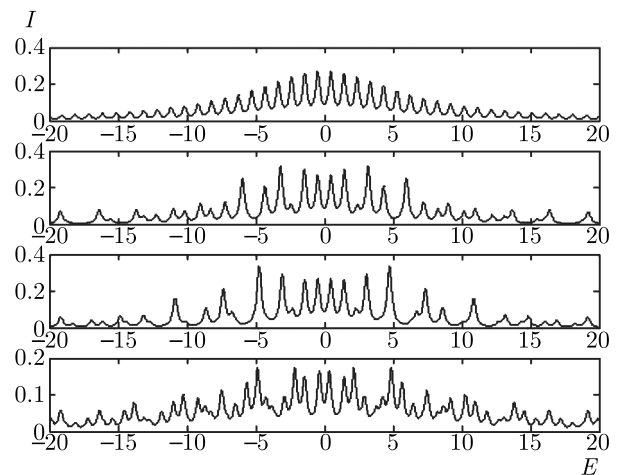


Fig. 3. Crossover from the regular to quasi-random spectrum of the mixed RS states upon the mixing deformation. $I(E)$ is the spectral density, and energy E is measured in the units of the interlevel spacing; K is sublattices spectra regular splitting, $K = 3$ in the computations; δ_1 and δ_2 are parameters which determine the additional (with respect to regular) sublattices splittings: $\delta_1 = 0, 0.1, 0.4, 0.7$ (from the top to the bottom), and $\delta_2 = 2\delta_1$; $C^2 = 0.1$

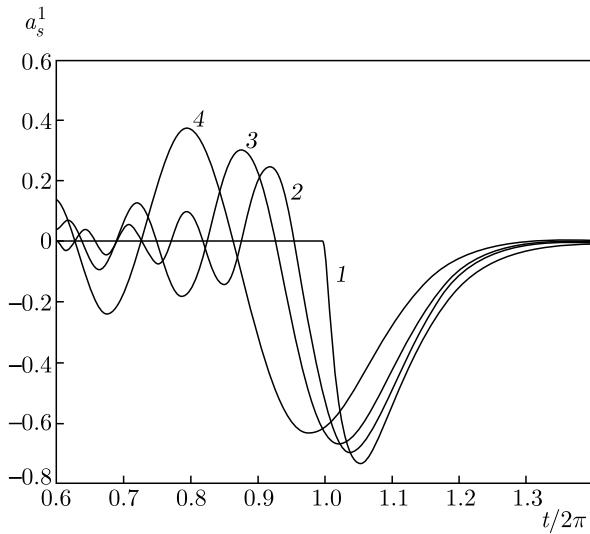


Fig. 4. Backward evolution of the initial state amplitude a_s^1 for the cycle $k = 1$. The reservoir possesses the increasing interlevel spacings. $C^2 = 1$. The model parameters describing the spectrum deformations are $b = 0$ and $a = 0, 0.15, 0.25, 0.35$ (curves 1–4, respectively)

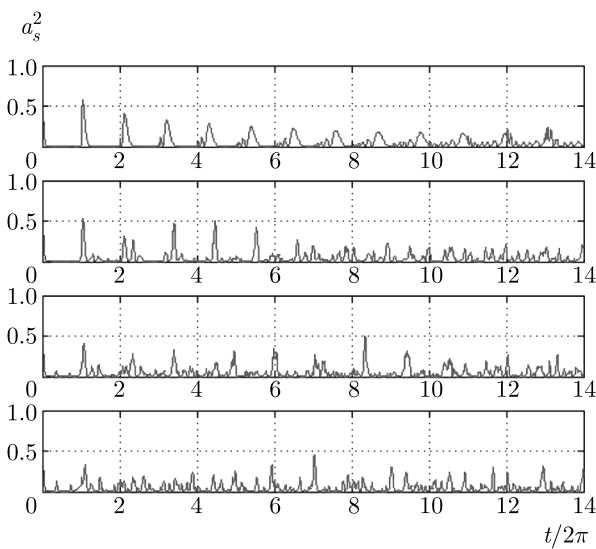


Fig. 5. Time evolution of the initial state coupled to reservoir with spectral mixing for the cycle $k = 1$: $C^2 = 1$, $K = 3$, $\delta_2 = 2\delta_1$, $\delta_1 = 0, 0.019, 0.049, 0.079$, $a = 0, 0.15, 0.25, 0.5$ (from the top to the bottom), and $b = 0$

Here we compile a brief self-contained review that we wish had existed when we first entered the field [2]. In what follows in the frame work of generalized Zwanzig approach, we study a number of nano-size quantum systems. Since our work is primary about physics (and only then how it can be modeled theoretically), it is worth to note first what are physical sys-

tems we have in mind. Our topic is nano-size quantum objects, possessing discrete vibrational energy spectra. Such objects are carbon nano-tubes, graphene flaks, metallic clusters, some large organic molecules or their clusters. Typical feature (relevant for everything what follows in the paper) of such systems is that their vibrational spectra are discrete and characteristic interlevel spacing $\bar{\Delta}$ is on the order of $0.1\text{--}10\text{ cm}^{-1}$. This value of $\bar{\Delta}$ is translated into the picosecond time scale for the periods of the recurrence cycles

$$T = \frac{2\pi}{c\bar{\Delta}} \simeq 10^{-10}\text{--}10^{-12}\text{ s},$$

where c is the light speed. In turn, experimental studies of the excited state evolution in large (nano-size) molecular systems [3–8] have established that the processes of vibrational relaxation, energy transfer, and ultra-fast chemical reactions occur in the same picosecond time range as recurrence cycles. Therefore, the recurrence cycles are essential ingredients to be included to describe theoretically such features of the quantum dynamics of nano-systems as irreversibility, chaotic behavior and loss-free distant energy transfer. These and some other high-resolution experiments (which will be cited and shortly discussed in our paper) demonstrate that a system initial vibrational state evolution, as a rule, has a complicated form with irregular oscillations. The methods of double resonances in the non-linear femtosecond spectroscopy [9–12] appear to be especially useful to observe these irregular oscillations of the initial and final state populations simultaneously. The phenomenon has been observed for the wide variety of large-size molecules in liquid and solid solutions and on interfaces [13–18]. Note to the point that irregular oscillations of the population of initially prepared excited state have been confirmed by the numerous quantum dynamical calculations [19–23].

The loss-free excitation energy transfer, observed in linear molecules consisting of 12–26 CH_2 fragments [20, 21], also belongs to a similar class of irregular in time behavior. In such kind of experiments, the initial excitation of the molecular terminal group produces the running wave with approximately constant speed (about of 2 ps per one fragment). Even more surprising is that instead of naively expected random distribution of the excitation energy over the total set of intra-molecular modes, the wave propagation lasts during several passages along the chain before the uniform distribution is established. The distant energy transfer occurs between localized vibrations of fragments separated by about 1 nm distance during 20–40 ps whereas the lifetime of these vibration excitations themselves

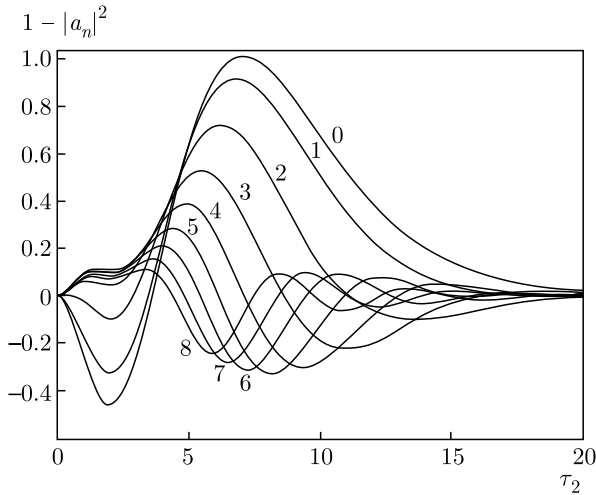


Fig. 6. Redistribution of the initial-state population over the mixed reservoir states with the amplitudes a_n during the second recurrence cycle $k = 2$ with duration τ_2 . The numbers of the reservoir states are shown near the curves

does not exceed 3 ps. The matter is that the excitation energy transfer includes intermediate excitations of delocalized long-lived vibrations binding the initial and final fragments [22–25].

These data permit to suggest that the irregular evolution is the generic property of the systems with dense discrete spectra. Therefore, the role of the reservoir with a discrete spectrum is fundamentally different from that with a continuous spectrum typical for macroscopic systems. In the latter case (with the infinite recurrence period time), the reservoir serves as a sink for energy flow. Contrary in the case of the discrete spectrum, repetitive reverse transitions from the reservoir to the initial state and in the opposite direction determine the non-trivial and often irregular long-time dynamics. The synchronization of these reverse transitions results in the appearance of a multi-component Loschmidt echo phenomenon with a partial recovery of the initial state population (at the frequency corresponding to the initial excited state energy), and double resonances (at the frequencies of the reservoir states). Both effects are responsible for non-monotonic time evolution. The counterpart of such behavior is the periodic energy concentration in one of the vibration mode, arising as a result of the time-dependent exchange between reservoir states far from equilibrium.

In a few of previous works of our group [2, 26–32], we illustrated how such complex behavior might appear in the frame work of the simple Zwanzig model, and how the simplest version of the model can be generalized to relax some unphysical assumptions of the

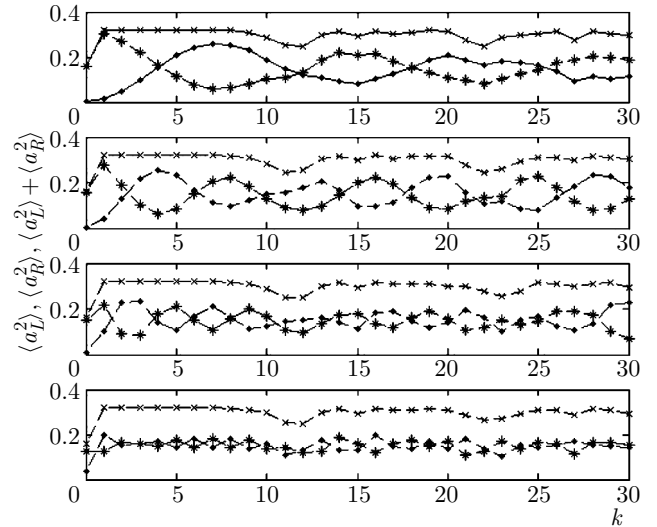


Fig. 7. Variation of the average per cycle populations of L_0 (\blacklozenge) and R_0 ($*$) states and the entire population of the two-level systems (\times) in the recurrence cycles versus the cycle number k : $C^2 = 1$ and the two-level splitting $\Delta = 0.4, 1.2, 2.7, 7.4$ (from the top to the bottom)

model. In these works, we also proposed a method which makes it possible to solve the dynamical problem analytically beyond the bare Zwanzig model approximations [27–32]. The main ingredient of our new method (only schematically and briefly described in the previous papers) is the representation of the partial amplitudes of recurrence cycles. Unlike the standard Fourier expansion over eigen-frequencies, this representation reveals explicitly the time dependent exchange between intramolecular states in each recurrence cycle. The fine structure of the Loschmidt echo arises as a result of the dephasing phenomena associated with the fact that the exchange of the different reservoir states with the initial state occurs not at the same instants of time. The synchronization of the reverse transitions is destroyed when the Loschmidt echo components of the different recurrence cycles start to overlap. The cycle overlapping determines the critical recurrence cycle number. Then at larger time (cycle numbers), the system dynamics is expected to be in the stochastic-like regime.

Since that time, we have realized that the quantum dynamics of nano-size systems is much richer than that predicted for the systems with continuous spectra, and that non-monotonous in time and irregular dynamics is a robust and generic feature of almost arbitrary quantum system with 10^2 – 10^4 degrees of freedom. Moreover, the regular-stochastic dynamic transition (crossover) yields to a loss of the expected one-to-

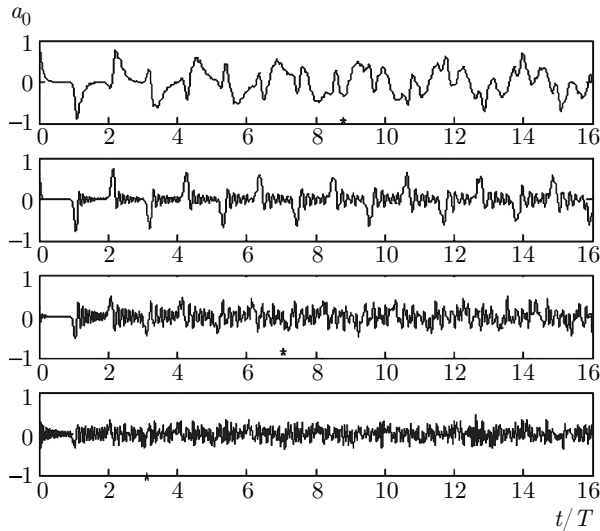


Fig. 8. Dynamics of the population at the excited impurity site located in the middle of the finite $N = 49$ size chain: a_0 is the amplitude of the initially excited site; $C^2 = 0.1, 0.25, 0.5, 0.95$ from the top to the bottom; the critical cycle number k_c is marked by the a star ($k_c = 23$ for $C^2 = 0.5$); T is the recurrence cycle period

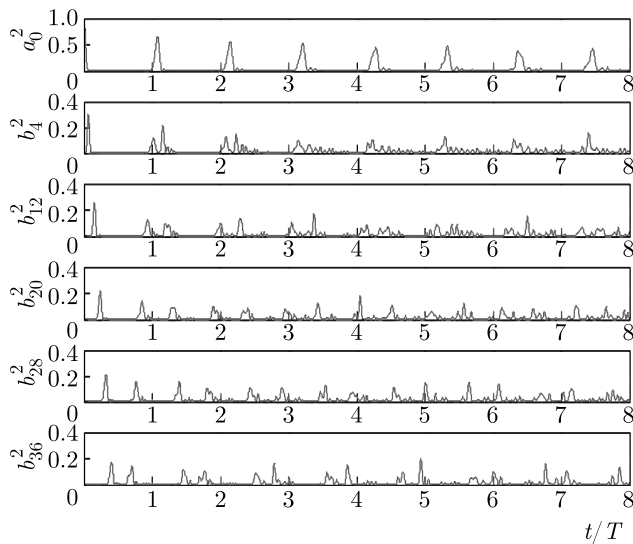


Fig. 9. Impurity site excitation propagated along the chain. $C^2 = 0.5, N = 49$. The site numbers are indicated on the panels as the subscripts of corresponding values along the vertical axes

one correspondence between system spectrum and its long-time dynamics. For all our examples, the spectrum remains deterministic, while long-time dynamics eventually becomes stochastic. This unusual combination is the specific feature of nano-systems.

Motivated by this new understanding, we decided to combine altogether our previous works to illustrate

our method on a number of particular physical realizations (only partially overlapping with those in the previous works). The aim to present this review arises from the conviction that unifying our previous works supplemented by the new applications of the developed theoretical approach and by new experimental data and observations collected in very recent year, yield to a new stage of development of this field: dynamics of nano-systems.

Our manuscript is divided into 7 sections. After this Introduction, in Sec. 2 of the full text of this paper, we summarize shortly the results on quantum dynamics of the bare Zwanzig model. A possible physical realization most closely satisfying the model assumptions is also discussed. Section 2 contains also an extended list of references to compensate partially its brevity. Then, in Sec. 3 utilizing developed in our works [27–32] theoretical approach, we investigate with all details the evolution of the population of the initially prepared single state of the system. In Sec. 4, we analyze various physically motivated generalizations of the bare Zwanzig model and how our analytical method should be modified to describe theoretically these generalizations. In the same section, we show that on the similar footing we can study dynamics not only for an individual (single) nano-system but as well for the ensemble of somehow distributed nano-systems. We investigate the reservoir states evolution in Sec. 5. We collect some already discussed in literature and new applications of our approach to physically interesting phenomena in nano-systems, namely, two-level systems coupled to reservoir, propagation of vibrational excitations in nano-size chains (Sec. 6). The last Sec. 7 summarizes the main findings of our work, with a discussion of possible physical consequences and interpretation of the results.

The results from the list of Refs. [1–69] are used or/and discussed in our work.

The figures illustrated our results are presented below.

Conclusion. Understanding all limitations of our simplified exactly solvable models, nevertheless we hope that the results collected in this review capture the essential peculiarities in nano-system dynamics. Namely, the dense discrete spectra characteristic for nano-particles and large-size molecules are responsible for appearance of recurrence cycles. By contrast to macroscopic systems with the continuous spectra, where the initial state population decreases monotonically in time, the Loschmidt echo and double resonances arise in each recurrence cycle. The revivals

in the time evolution makes it possible the emergence of new mechanisms of vibration stimulated processes in single nano-particles and their ensembles as well. The regular behavior in the initial recurrence cycles transformed into chaotic-like long-time evolution is an inherent characteristic of nano-world. The combination of the deterministic spectra with chaotic-like long-time dynamics has no analogs in the quantum dynamics of the macroscopic dissipative systems. Owing to specific mechanisms of energy transfer and redistribution within the manifold of intramolecular modes, the loss-free and distant energy transfer becomes possible. The unique property of nano-systems is the possibility for periodical accumulation of the energy on the selected vibrational modes. The new fields for experimental studies and applications of this unusual effect are opened.

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