Quantum dynamics for an initial vibrational level \(\varepsilon_s^0\) coupled to a set of discrete dense levels \(\varepsilon_n^0\) can be described in a framework of the so-called spin-boson Hamiltonian [1, 2]

\[
H = \varepsilon_s^0 b_s^+ b_s + \sum_n \varepsilon_n^0 b_n^+ b_n + \sum_n C_n (b_n^+ b_s + b_s^+ b_n),
\]

where \(b_s^+ (b_s)\) is initial level creation (annihilation) operator (i.e., excitation of the initial vibrational level from the system ground state, which is assumed so deep that its influence on the system dynamics can be neglected), and \(b_n^+ (b_n)\) are similar operators for the discrete reservoir levels. \(C_n\) stands for the coupling matrix elements. For this Hamiltonian time dependent wave function can be presented in a series over full orthogonal set of wave functions of the unperturbed (uncoupled) initial and reservoir states with time dependent coefficients (amplitudes) \(a_s(t)\)

\[
a_s(t) = \sum_n \left\{ \frac{dF}{dE} \right\}^{-1} \exp(-iEt) \bigg|_{E = \varepsilon_n},
\]

where \(F(E) = 0\) is a secular equation to find the eigenstates \(n\) of Hamiltonian (1).

Common wisdom [3–6] claims that stochastic-like dynamics is a feature typical for random matrix Hamiltonians, with random eigenstate spectra. However for a system with discrete dense spectrum (e.g., vibrational states in nanoparticles or medium size molecules) there is another dynamic root to quasi-stochastic behavior. Indeed for such a system with discrete spectrum, dynamic evolution is represented by periodically repeating steps (recurrence cycles). When time is going on, the initial vibrational level population oscillates faster and faster and corresponding response signals become broader. Eventually at a certain critical cycle number \(k_c\), the cycles are overlapped in time. Then for any finite accuracy of time or frequency measurements, time evolution looks as irregular, quasi-stochastic, and indistinguishable from truly chaotic behavior. It was demonstrated recently [7–9] for the simplest version of the spin-boson Hamiltonian (1) with \(\varepsilon_n^0 = n\) and \(C_n = C\) (so-called Zwanzig approximation [10]). Here (and in what follows) we utilize a characteristic reservoir spacing as energy unit, and \(n = 0\) is the reservoir level coinciding with \(\varepsilon_s^0\). It is worth noting that this dynamic mixing occurs in a single Hamiltonian system (not for an ensemble of equivalent systems).

Since there are mentioned above two roots to stochastic-like time evolution, two natural questions arise, namely, (i) how the both mechanisms are inter-related, and (ii) whether they are independent ones.

In the framework of a simple spin-boson Hamiltonian we study an interplay between dynamic and spectral roots to stochastic-like behavior. The Hamiltonian describes an initial vibrational state coupled to discrete dense spectrum reservoir. The reservoir states are formed by three sequences with rationally independent periodicities 1, 1 ± \(\delta\) typical for vibrational states in many nanosize systems (e.g., large molecules containing CH\(_2\) fragment chains, or carbon nanotubes). We show that quantum evolution of the system is determined by a dimensionless parameter \(\delta \Gamma\), where \(\Gamma\) is characteristic number of the reservoir states relevant for the initial vibrational level dynamics. When \(\delta \Gamma > 1\) spectral chaos destroys recurrence cycles and the system state evolution is stochastic-like. In the opposite limit \(\delta \Gamma < 1\) dynamics is regular up to the critical recurrence cycle \(k_c\) and for larger \(k > k_c\) dynamic mixing leads to quasi-stochastic time evolution. Our semi-quantitative analytic results are confirmed by numerical solution of the equation of motion. We anticipate that both kinds of stochastic-like behavior (namely, due to spectral mixing and recurrence cycle dynamic mixing) can be observed by femtosecond spectroscopy methods in nanosystems in the spectral window \(10^{11}–10^{13} \text{ s}^{-1}\)

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To answer these questions is a purpose of our presentation. We study quantum dynamics for a version of spin-boson Hamiltonian (1), where the both ingredients yielding to stochastic time evolution (spectral and dynamic) may be presented simultaneously and can be tuned by model Hamiltonian parameters. We assume that the reservoir discrete bare spectrum in Hamiltonian (1) is formed by three equidistant sequences with different periods

\[ \varepsilon_n^0 = \pm 3n; \quad \varepsilon_1^0 = \pm (1 - \delta)(3n + 1); \quad \varepsilon_2^0(n) = \pm (1 + \delta)(3n + 2), \]

where spectral shift dimensionless parameter \( \delta \leq 1/2 \). It is worth noting that such kind of triplet structures are quite frequently observed in the spectra of many molecular systems, forming notorious Snyder sequences [11] (see also more recent publications on high resolution spectroscopy of nanotubes [12], phospholipid molecules [13, 14] and fullerenes [15]).

When the total number of levels \( N \to \infty \) and the sequence periods \( 1, 1 \pm \delta \) are rationally independent, the spectrum of the reservoir becomes mixed. In own turn, according to the ergodic properties [16, 17] chaotic behavior of an ensemble of systems (random eigenvalue distribution) holds if its individual system is mixing. That is why we term our case as exhibiting of stochastic-like behavior (cf. with definition [18]).

In more practical terms mixing phenomenon can be related to reservoir level ordering. Indeed, level ordering and interlevel spacings depend on a cycle number. In a zero cycle the spectrum is formed by triplets in the following sequence

\[ \varepsilon_2(n - 1) < \varepsilon_0(n) < \varepsilon_1(n) < \varepsilon_2(n). \]

When \( n \) increases the quantities \( p_1^{(0)} = \varepsilon_0(n) - \varepsilon_2(n - 1) \) and \( p_2^{(0)} = \varepsilon_0(n) - \varepsilon_0(n) \) become smaller and fill with a step \( 3\delta \) intervals \([0, 1 \pm \delta]\). Level splitting between neighboring triplets \( p_3^{(0)} = \varepsilon_1(n) - \varepsilon_0(n) \) increases with a step \( 6\delta \) approaching to 3. In the next cycle \( k = 1 \) the level ordering is different

\[ \varepsilon_1(n) < \varepsilon_0(n) < \varepsilon_2(n - 1) < \varepsilon_1(n + 1), \]

and the quantities \( p_1^{(1)}(n) = \varepsilon_2(n - 1) - \varepsilon_0(n) \) and \( p_2^{(1)}(n) = \varepsilon_0(n) - \varepsilon_1(n) \) are increased with the same as in the \( k = 0 \) cycle, step \( 3\delta \) up to a limit value \( 3/2 \). One can check that in the next even cycles the splittings \( p_1^{(2k)} \) and \( p_2^{(2k)} \) decrease, whereas \( p_3^{(2k)} \) increases. In the odd cycles the opposite variation of the splittings hold (\( p_1 \) and \( p_3 \) increase, and \( p_2 \) decreases). Eventually levels from different triplets fill in the \( k \to \infty \) limit almost uniformly and densely the interval \([0, 6\delta]\) with odd-even alternations with the recurrence cycle number. By rather lengthy and boring but straightforward calculations we find that for cycle number \( k \geq 1 \), the variables \( p_1 \) and \( p_2 \) fill uniformly the intervals

\[ \left[ \frac{3}{2} - a_{k+1}, a_k^{(1)} \right]; \quad \left[ \frac{3}{2} - a_{k+1}, a_k^{(2)} \right], \]

with the different order of \( p_1 \) and \( p_2 \) in even and odd cycles. The \( p_3 \) fills the interval

\[ \left[ 3 - a_k^{(3)}, a_k^{(3)} \right]. \]

In own turn the above intervals limits \( a_k^{(j)} \) with \( j = 1, 2, 3 \) satisfy the following relations

\[ a_k^{(1, 2)} = \left\{ \frac{1}{6\delta} (3k + 2) \pm \frac{1}{3} \right\}; \]

\[ a_k^{(3)} = \left\{ \frac{1}{6\delta} (3k + 2) - \frac{1}{2} \right\}, \]

where \( \{X\} \) stands for the fractional part of \( X \). At \( k \gg 1 \) the \( (8) \) can be generated approximately by so-called fractional part recurrence relation

\[ a_{k+1} = \left\{ \frac{1}{2\delta} a_k \right\}. \]

As it is known [19] the fractional part transformation is the mixing one (i.e., stochastic) with characteristic correlation time (in our notation) \( \propto \ln(1/\delta) \). Thus our model reservoir spectrum is the reservoir with spectral mixing. This phenomenon can be formulated as the mixing of \( p_j \) parameters within the interval \([0, 3]\). The interlevel spacing distribution density is approximately (over the parameter \( 1/N \)) a constant \( \approx 5/9 \) in the interval \([0, 3/2]\) and another constant \( \approx 1/9 \) in the interval \([3/2, 3]\). Without going to more subtle mathematical details of random sequences we calculate numerically the distribution function \( \rho(\varepsilon) \) for our model spectrum. When the total number \( N \) of the reservoir levels increases the distribution approaches to that with two uniformly distributed parts (see the Fig. 1, where we show also the widely used in the literature Wigner distribution (see e.g., [5, 6], and also [20]) which holds for orthogonal Gaussian random matrices [5]).

Let us come back to the secular equation to find the eigenstates

\[ F(\varepsilon) = \varepsilon \]

\[ \sum_{n = -N}^{n = +N} \left( \frac{C_{3n}^2}{\varepsilon - \varepsilon_{3n}} + \frac{C_{3n+1}^2}{\varepsilon - \varepsilon_{3n+1}} + \frac{C_{3n+2}^2}{\varepsilon - \varepsilon_{3n+2}} \right) = 0. \]

For the ease of algebra (if needed this approximation can be relaxed) we assume following Zwanzig [10] approximation

\[ C_{3n} = C_{3n+1} = C_{3n+2} = C. \]