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SCATTERING, TRANSPORT & STOCHASTICITY IN QUANTUM SYSTEMS

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I. INTRODUCTION

Recent work has shown the importance of chaotic behavior and of the sensitivity to initial conditions to understand how irreversible processes such as diffusion, viscosity, heat conductivity or reactions may arise in classical Hamiltonian systems [1, 2]. Indeed, the exponential separation between classical trajectories which are infinitesimally close can be shown to have for consequence exponential decays or relaxations in the Hamiltonian scattering by a hill, in some chaotic scattering systems, or in simple fully chaotic maps such as the multibaker map [2].

Moreover, in the escape-rate formalism, the transport coefficients have been shown to be related to the difference between the sum of positive Lyapunov exponents – which characterize the sensitivity to initial conditions – and the Kolmogorov-Sinai (KS) entropy – which characterizes the dynamical randomness of the trajectories that are trapped forever in the scattering region and that form a so-called fractal repeller [3–6].

These results and others [7–11] suggest that the microscopic chaos in the motion of atoms or molecules composing matter plays an important role in the transport and reaction properties of classical dynamical systems.

However, the question arises whether these considerations about classical chaos are still relevant at the quantum-mechanical level of description. The reason is that quantum mechanics is a linear theory although classical mechanics is nonlinear. This problem has been the subject of much work for about two decades and many results have accumulated which provide a rich and detailed picture of the properties of classically chaotic quantum systems.

In order to connect quantum to classical mechanics and to study how chaotic behavior may emerge at the classical level, a method of choice is the semiclassical theory in which the quantum-mechanical properties are expanded asymptotically in the formal limit where the Planck constant vanishes $\hbar \to 0$. A central result of modern semiclassical theory is the famous Gutzwiller trace formula [12] which allows the periodic-orbit quantization of classically chaotic systems and, in particular, of scattering systems such as the disk scatterers [13], the helium atom [14, 15] and the hydrogen negative ion [16], as well as metastable triatomic molecules [17]. Although practically limited to few-body systems, the semiclassical quantization method already allows us to study irreversible decay processes such as electronic conductance, unimolecular reactions or atomic auto-ionizations.

Spatially extended scattering systems have also been studied in order to characterize the transport across these systems from the viewpoint of scattering theory. In particular, Landauer proposed a scattering theory of electronic conductance which is powerful for the mesoscopic semiconductor circuits. Beside conductance which is obtained from the transmission coefficient in Landauer's theory, time-dependent properties of relaxation type are also of great interest because they are related to the diffusion coefficient in the quasiclassical limit.

In Sections 2 and 3, we shall give an overview of the methods of semiclassical quantization and of some of its applications to scattering systems.

In Section 4, we shall be concerned by relaxation and dynamical randomness in many-body quantum systems. It turns out that quantum systems acquire some of the dynamical properties of classical chaotic systems in the large-system limit or thermodynamic limit. In this limit, several types of properties may be studied such as the statistical properties of the energy eigenvalues and eigenfunctions. Much work has been devoted to these spectral properties showing that many quantum systems with a sufficient degree of genericity behaves like random matrices on the small energy scale where individual eigenvalues are resolved [18, 19]. Such considerations were initiated by Wigner and others in the fifties in the context of nuclear physics [18]. Today, these random-matrix properties have been experimentally observed also in atomic, molecular, electromagnetic, and acoustic systems. Besides, several numerical calculations have shown that many-body quantum systems of solid-state physics behave similarly. We shall here review such results for many-spin quantum systems [20]. These random-matrix properties are also observed in classical chaotic systems and they allow to justify some of the basic laws of thermostatics. In particular, Srednicki has shown that some of the statistical properties of eigenfunctions of classically chaotic systems imply thermalization and the quantum equilibrium thermal distributions [21]. These properties can also justify dynamical properties such as the decay of time correlation functions evaluated with typical eigenfunctions. In this context, a nonMarkovian stochastic Schrödinger equation has recently been derived on the basis of similar and related considerations [22].

Finally, we shall be concerned by the characterization of dynamical randomness in large quantum systems and by the definition of quantum analogues of the dynamical entropies per unit time.

II. SEMICLASSICAL QUANTIZATION

A. Quantum time evolution of pure states

In quantum mechanics, a system is described by a wavefunction which evolves in time according to the linear Schrödinger equation

$$i\hbar \, \partial_t \, \psi \;=\; H \, \psi \; . \tag{1}$$

If the Hamiltonian H is time independent, the wavefunction at the current time t is given by applying the time evolution operator to the initial wavefunction

$$\psi_t \;=\; \exp(-iHt/\hbar) \; \psi_0 \; . \tag{2}$$

In the position representation, this equation has the following integral form

$$\psi_t(\mathbf{q}) \;=\; \int d\mathbf{q}_0 \; K(\mathbf{q},\mathbf{q}_0,t) \; \psi_0(\mathbf{q}_0) \; . \tag{3}$$

where $K(\mathbf{q},\mathbf{q}_0,t)$ is the propagator that is the probability amplitude for the particle to move between the positions $\mathbf{q}_0$ and $\mathbf{q}$ during the time t.

Feynman has shown that the quantum propagator – which is the time evolution operator in the position representation – can be obtained by a path integral involving the Lagrangian function $L(\mathbf{q},\dot{\mathbf{q}},t)$ of the system as

$$K(\mathbf{q},\mathbf{q}_0,t) = \langle \mathbf{q} | \exp(-iHt/\hbar) | \mathbf{q}_0 \rangle = \int \mathcal{D}\mathbf{q}(t) \;\; \exp \frac{i}{\hbar} \int_0^t L(\mathbf{q},\dot{\mathbf{q}},\tau) d\tau \; , \tag{4}$$

for the propagation from $\mathbf{q}_0$ to $\mathbf{q}$ during the time t.

If the propagation proceeds in the semiclassical regime, the action may be supposed to be much larger than the Planck constant

$$W = \int_0^t L(\mathbf{q},\dot{\mathbf{q}},\tau) d\tau \gg \hbar \; . \tag{5}$$

In this semiclassical limit, the path integral can be evaluated by the method of stationary phases, which selects the preferred paths for the propagation as the classical trajectories which are the rays obeying the Hamiltonian equations

$$\dot{\mathbf{q}} \;=\; + \, \frac{\partial H_{\rm cl}}{\partial \mathbf{p}} \; , \qquad \text{and} \qquad \dot{\mathbf{p}} \;=\; - \, \frac{\partial H_{\rm cl}}{\partial \mathbf{q}} \; . \tag{6}$$

The propagator can thus be asymptotically approximated by a sum over all the classical trajectories ℓ which connects $\mathbf{q}_0$ to $\mathbf{q}$ during the time t

$$K(\mathbf{q},\mathbf{q}_0,t) \;\simeq_{\hbar\to 0}\; \sum_\ell \; \mathcal{A}_\ell(\mathbf{q},\mathbf{q}_0,t) \; \exp \frac{i}{\hbar} W_\ell(\mathbf{q},\mathbf{q}_0,t) \; . \tag{7}$$

Since the propagator $K(\mathbf{q},\mathbf{q}_0,t)$ is still a quantum amplitude it is given by the linear superposition of the quantum amplitudes of the different classical trajectories. W_ℓ is the action of the classical trajectory and $\mathcal{A}_\ell$ is an amplitude associated with the classical trajectory, the expression of which can be found elsewhere [23]. This amplitude behaves differently depending on the stability properties of the classical trajectory. We may say that, globally over a long time interval, the more unstable the trajectory is the faster its amplitude decays.

B. Quantum time evolution of mixed states

In order to consider a statistical ensemble of pure quantum states, we introduce the density matrix $\rho = \sum_i \vert\psi_i\rangle p_i \langle\psi_i\vert$, where p_i are the probabilities of occurrence of the states ψ_i in the statistical ensemble. The average of an observable D is then given in terms of this density matrix by $\langle D\rangle = \mathrm{tr}\rho D$. The time evolution of the density matrix is governed by the Landau-von Neumann or quantum Liouvillian operator

$$\partial_t \,\rho \; = \; \frac{1}{i\hbar}[H,\rho] \; = \; \mathcal{L}\rho \; . \tag{8}$$

An important related superoperator is the energy superoperator

$$\mathcal{H}(\cdot) \; = \; \frac{1}{2}(H\,\cdot \; + \; \cdot\, H) \; . \tag{9}$$

The energy superoperator always commutes with the Liouvillian superoperator $[\mathcal{L},\mathcal{H}]=0$, so that they have common eigenstates such that

$$\begin{cases} \mathcal{L}\rho = s\rho \; , \\ \mathcal{H}\rho = E\rho \; , \end{cases} \tag{10}$$

where is is a complex frequency and E an energy. For a bounded quantum system, these common eigenstates are given by $\rho_{mn} = \vert E_m\rangle\langle E_n\vert$ in terms of the energy eigenstates, $H\vert E_n\rangle = E_n\vert E_n\rangle$.

In order to consider a representation which is close to the classical phase-space representation, we can introduce the Wigner transform of an operator X by

$$X_{\mathrm{W}}(\mathbf{q},\mathbf{p}) \; = \; \int d^f r \;\; \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar) \; \left\langle \mathbf{q}-\frac{\mathbf{r}}{2}\middle\vert X \middle\vert \mathbf{q}+\frac{\mathbf{r}}{2}\right\rangle \; . \tag{11}$$

In the Wigner representation, the Liouvillian and energy superoperators are given by [24]

$$\begin{cases} (\mathcal{L}\rho)_{\mathrm{W}} = \frac{2}{\hbar}\; H_{\mathrm{W}} \;\; \sin\frac{\hbar\hat{\Lambda}}{2} \;\; \rho_{\mathrm{W}} = \left(\mathcal{L}_{\mathrm{cl}} + \hbar^2\mathcal{L}^{(2)} + \hbar^4\mathcal{L}^{(4)} + \cdots\right)\rho_{\mathrm{W}} \; , \\ (\mathcal{H}\rho)_{\mathrm{W}} = H_{\mathrm{W}} \;\; \cos\frac{\hbar\hat{\Lambda}}{2} \;\; \rho_{\mathrm{W}} = \left(H_{\mathrm{cl}} + \hbar^2\mathcal{H}^{(2)} + \hbar^4\mathcal{H}^{(4)} + \cdots\right)\rho_{\mathrm{W}} \; , \end{cases} \tag{12}$$

where $\hat{\Lambda} = \overleftarrow{\partial_{\mathbf{q}}}\;\overrightarrow{\partial_{\mathbf{p}}} \; - \; \overleftarrow{\partial_{\mathbf{p}}}\;\overrightarrow{\partial_{\mathbf{q}}}$, $H_{\mathrm{W}} = H_{\mathrm{cl}}$ is the classical Hamiltonian, while

$$\mathcal{L}_{\mathrm{cl}}(\cdot) \; = \; \{H_{\mathrm{cl}}, \; \cdot\;\}_{\mathrm{Poisson}} \tag{13}$$

is the classical Liouvillian operator given by the Poisson bracket with the Hamiltonian.

These results lead to the most interesting observation that the energy superoperator becomes an operator of multiplication with the classical Hamiltonian at the leading order of an expansion in powers of the Planck constant. In the quasiclassical limit, if we consider the eigenstates of the energy superoperator they must therefore satisfy

$$\left[H_{\mathrm{cl}} + \mathcal{O}(\hbar^2)\right] \;\; \rho_{\mathrm{W}} \;\; = \;\; E\;\rho_{\mathrm{W}} \; . \tag{14}$$

If the corrections in $\hbar^2$ can be neglected, we have an equation of the form $xf(x)=0$ for an unknown density $f(x)$ depending on the energy variable $x = E - H_{\mathrm{cl}}$. Such an equation has a solution in the theory of generalized functions or Schwartz distributions, which is given by the Dirac distribution $f(x) = \delta(x)$ up to a constant factor. We can therefore conclude that, in the quasiclassical limit, the eigenstate is defined on the energy shell $H_{\mathrm{cl}} = E$ by

$$\rho_{\mathrm{W}} \;\; = \;\; g\;\delta(E - H_{\mathrm{cl}}) \;\; + \;\; \mathcal{O}(\hbar^2) \; , \tag{15}$$

where $g(\mathbf{q},\mathbf{p})$ is some density which may be proportional to other delta distributions involving further constants of motion.

If we consider an eigenstate with the eigenvalue $s=0$ for the Liouvillian operator and if the system is ergodic, the function g is constant and we recover the microcanonical ensemble in the quasiclassical limit $\hbar \to 0$. This result is related to a conjecture by Berry and Voros [25] that averages over the Hamiltonian eigenstates, $\langle E_n\vert A\vert E_n\rangle$, tend to the microcanonical average in the limit $\hbar \to 0$. This conjecture has been proved for certain classically chaotic systems which are ergodic, mixing and hyperbolic of Anosov type [26].

The time-dependent properties of a system can be characterized by the time correlation functions of the various observables of the system, such as the autocorrelation function of D

$$C(t) \; = \; \langle D(0)D(t)\rangle \; , \quad \text{with} \quad D(t) = \exp(iHt/\hbar) \; D \; \exp(-iHt/\hbar) \; , \tag{16}$$

where the average is taken over a time-invariant state which is either a Hamiltonian eigenstate or a mixed state given by a density matrix which is a function of the Hamiltonian operator: $\rho = \mathcal{P}(H)$. It is also interesting to introduce the spectral functions that are the Fourier transforms of the correlation functions

$$S(\omega) \; = \; \int_{-\infty}^{+\infty} dt \; \exp(-i\omega t) \; \langle D(0)D(t)\rangle \; . \tag{17}$$

An example of such a spectral function is the cross-section for photoabsorption that is given by the Fourier transform of the time autocorrelation function of the dipole electric moment of the system [27]. The average is taken over the quantum state of the system prior to the absorption. If the system is at a low temperature with respect to the energy of the absorbed photon, the initial system can be considered in its ground state. This case is treated in the following Subsection 2.3. However, if the temperature is higher, the initial state is a thermal state described by a density matrix and a different treatment is required which is described in Subsection 2.4.

C. Trace formula for pure-state averaging

In this subsection, our aim is to obtain a semiclassical expression for the spectral function (17) in the case where the average is carried out over a pure state of density matrix $\rho = |\varphi_0\rangle\langle\varphi_0|$ which projects on the ground Hamiltonian eigenstate: $H|\varphi_0\rangle = E_0|\varphi_0\rangle$.

In this case, the spectral function (17) becomes

$$S(\omega) = \text{tr} \; A \; \delta(E_0 + \hbar\omega - H) \qquad \text{with} \qquad A = 2\pi\hbar \; D|\varphi_0\rangle\langle\varphi_0|D \; . \tag{18}$$

Therefore, at low temperatures, the spectral function is expressed as a trace of an operator directly involving a lone resolvent of the Hamiltonian. Such an expression can be calculated semiclassically and expanded in terms of periodic orbits with the Gutzwiller trace formula.

We owe to Gutzwiller the first derivation of a semiclassical trace formula including the oscillating contributions of the classical periodic orbits for quantities like (18) [12]. Under certain circumstances, the periodic-orbit contributions are able to approximate semiclassically the effect of quantization. Previously, the work by Weyl and Wigner showed how to approximate quasiclassically expressions given by traces [24]. Such quasiclassical expansions are based on the use of the Wigner transform (11). However, such quasiclassical expansions do not reproduce the effect of quantization. Gutzwiller derived a periodic-orbit trace formula for the level density which is defined by Eq. (18) with A replaced by the identity operator I. The trace has for effect that the selected classical trajectories are closed, i.e., are periodic orbits. However, Gutzwiller's treatment is general and extends also to the spectral functions for which we can obtain the following semiclassical approximation [23, 28]:

$$\begin{aligned} S(\omega) \; &= \; \int \frac{d^f q d^f p}{(2\pi\hbar)^f} \; A_{\rm W}(\mathbf{q},\mathbf{p}) \; \delta\left[E - H_{\rm cl}(\mathbf{q},\mathbf{p})\right] + \mathcal{O}(\hbar^{-f+1}) \\ &+ \; \frac{1}{\pi\hbar} \; \sum_p \sum_{r=1}^{\infty} \left(\oint_p A_{\rm W} dt \right) \frac{\cos\left[\frac{r}{\hbar} S_p(E) - r\frac{\pi}{2}\mu_p\right]}{|\det(\mathbf{m}_p^r - \mathbf{I})|^{1/2}} + \mathcal{O}(\hbar^0) \; , \end{aligned} \tag{19}$$

with $E = E_0 + \hbar\omega$. In this formula, $A_{\rm W}$ denotes the Wigner transform (11) of the operator A defined in Eq. (18);

$$S_p(E) \; = \; \oint_p \mathbf{p} \cdot d\mathbf{q} \tag{20}$$

is the reduced action of the periodic orbit p; μ_p is its Maslov index which characterizes the winding of the trajectories around the periodic orbit and $\mathbf{m}_p$ is the matrix of the linearized Poincaré map near the periodic orbit. The sum is carried out over all the prime periodic orbits and their repetition $r = 1, 2, 3, ...$ The period of the periodic orbit is given in terms of the reduced action (20) according to

$$T_p(E) \; = \; \frac{\partial S_p(E)}{\partial E} \; . \tag{21}$$

With the formula (19), the spectral function is decomposed into a smooth quasiclassical background given by the first term and oscillating contributions from the periodic orbits which are superposed on top of the smooth background. The peaks of the spectral function may allow us to identify the energy eigenstates of the system.

It turns out that the contribution of the unstable periodic orbits to the spectral function can be rewritten as

$$S(\omega)\Big|_{\rm po} = \frac{1}{\pi}\ {\rm Im}\frac{\partial}{\partial\lambda}\ln\tilde{Z}(E,\lambda)\Big|_{\lambda=0} \ +\ \mathcal{O}(\hbar^0)\ , \tag{22}$$

with $E = E_0 + \hbar\omega$, in terms of the so-called Selberg Zeta function

$$\tilde{Z}(E,\lambda)\ =\ \prod_p \prod_{m_1,\ldots,m_{f-1}=0}^{\infty} \left\{ 1\ -\ \frac{\exp\left[\frac{i}{\hbar}\tilde{S}_p(E,\lambda) - i\frac{\pi}{2}\mu_p\right]}{\prod_{k=1}^{f-1} |\tilde{\Lambda}_p^{(k)}(E,\lambda)|^{\frac{1}{2}}\,\tilde{\Lambda}_p^{(k)}(E,\lambda)^{m_k}} \right\}\ , \tag{23}$$

which is a product over the periodic orbits of the perturbed Hamiltonian system, $\tilde{H}_{\rm cl}(\mathbf{q},\mathbf{p},\lambda) = H_{\rm cl}(\mathbf{q},\mathbf{p}) + \lambda A_{\rm W}(\mathbf{q},\mathbf{p})$ [23, 29]. In the Zeta function (23), the stability factors $\tilde{\Lambda}_p^{(k)}(E,\lambda)$ are the eigenvalues of the linearized Poincaré map $\tilde{\mathbf{m}}_p(E,\lambda)$ and they satisfy $|\tilde{\Lambda}_p^{(k)}| > 1$. If the classical system is structurally stable, we have that $S_p(E) = \lim_{\lambda\to 0}\tilde{S}_p(E,\lambda)$. The product over the periodic orbits can be expanded into a sum over topological combinations of all the periodic orbits, called the cycle expansion [30, 31]. By regrouping terms of high period, this series can be reordered into terms of lower and lower magnitudes as the period increases. Truncation can be carried out for numerical computations [31].

The presence of several periodic orbits leads to interferences between their different quantum amplitudes in the cycle-expanded Zeta function. These interferences cause irregularities in the structures of the spectral function. The greater is the number of periodic orbits with different reduced actions, the greater are the irregularities in the spectral function [32].

D. Trace formula for mixed-state averaging

Let us now consider that the spectral function involves an average over a statistical mixture described by a density matrix which is a function of the Hamiltonian operator $\rho = \mathcal{P}(H)$. This is the case for a canonical ensemble for which $\mathcal{P}(E) = \exp(-\beta E)/Z$ with the inverse temperature β.

The spectral function (17) can be expressed as

$$S(\omega) = \int dt\ dE\ {\rm e}^{-i\omega t}\ \mathcal{P}(E)\ {\rm tr}\ \delta(E-H)D(0)D(t)\ , \tag{24}$$

in terms of a time autocorrelation function averaged over a microcanonical ensemble. By using the Wigner transform and the Gutzwiller trace formula, the spectral function can be semiclassically approximated as [33, 34]

$$\begin{aligned} S(\omega)\ &=\ \int dt \int \frac{d^f x d^f p}{(2\pi\hbar)^f}\ \mathcal{P}(H_{cl})\ D_{\rm W}\ {\rm e}^{(\mathcal{L}_{cl}-i\omega)t} D_{\rm W} + \mathcal{O}(\hbar^{-f+1}) \\ &+\ \frac{2}{\hbar}\sum_{p,r,n} \mathcal{P}_{p,n}\,|D_{p,n}|^2\ \left|\frac{dS_{p,n}}{d\omega}\right|\ \frac{\cos\left(\frac{r}{\hbar}S_{p,n} - r\frac{\pi}{2}\mu_p\right)}{|\det(\mathbf{m}_{p,n}^r - \mathbf{I})|^{1/2}} + O(\hbar^0), \end{aligned} \tag{25}$$

where all the quantities in the periodic-orbit contributions are evaluated at the energies $E = E_{p,n}(\omega)$ at which there is resonance between the driving frequency ω and the intrinsic frequency of the periodic orbit p: $\omega = 2\pi n/T_p(E)$. The first term of (25) is the classical expression involving the classical Liouvillian operator. $D_{\rm W} = D_{\rm W}(\mathbf{q},\mathbf{p})$ is the Wigner transform of the operator D while $H_{\rm cl}$ is the classical Hamiltonian. The second term contains the oscillating contributions of each unstable periodic orbit p at repetition r. The magnitude of each periodic-orbit contribution is proportional to the square of the coefficient of the Fourier expansion of the observable $D_{\rm W}$ evaluated at the periodic orbit p

$$D_{p,n} = \frac{1}{T_p}\int_0^{T_p} D_{\rm W}\left[\mathbf{q}(t),\mathbf{p}(t)\right]\ \exp\left(-i\frac{2\pi n}{T_p}t\right)\ dt\ . \tag{26}$$

$\mathbf{m}_{p,n}$ is the same matrix of the linearized Poincaré map of the periodic orbit p at the energy $E = E_{p,n}(\omega)$ [33].

We observe that, here again, the spectral function has a smooth background given by the quasiclassical expression while the oscillating contributions from the periodic orbits are superposed on top of this smooth background because the system is finite. The same semiclassical calculation can be carried out for the dynamic susceptibility of a non-interacting system of Fermions in a trapping potential [33]. In this example, the oscillating contributions are due to the Fermionic shells which exist in atoms, in nuclei or in metallic clusters. These periodic-orbit corrections prevent the existence of normal dissipation or transport, but since they only appear $\hbar^{f-1}$ away from the leading quasiclassical term these oscillating contributions tend to disappear when the number of degrees of freedom f increases indefinitely so that we may expect that normal dissipation or transport is restored when $f = \infty$.

The comparison with Eq. (19) shows that a very different expression for the spectral function is obtained here in the case of a state given by the statistical mixture. Here, we find a non-trivial time dependence under the classical dynamics involving a statistical ensemble of trajectories according to the density $\mathcal{P}(H_{\rm cl})$. For a classically mixing system, the autocorrelation function is expected to decay for $t \to \pm\infty$. This decay is controlled by classical resonances called the Pollicott-Ruelle resonances which are the generalized eigenvalues of the classical Liouvillian operator [35]. These resonances are given by taking the trace of the Frobenius-Perron operator $\exp(\mathcal{L}_{\rm cl}t)$ over the energy shell $H_{\rm cl} = E$. We can view this trace of a classical operator as the quasiclassical limit of an appropriate trace of the quantum Liouvillian evolution operator restricted to the eigenstates of the energy superoperator. Using a result by Cvitanovic and Eckhardt for the trace of the classical Frobenius-Perron operator in a classically hyperbolic system with unstable periodic orbits [36], we find that the trace of the quantum Liouvillian evolution operator is approximated quasiclassically by

$$\mathrm{Tr}_E \ \exp(\mathcal{L}t) \ = \ \sum_p \sum_{r=1}^{\infty} T_p \ \frac{\delta(t - rT_p)}{|\det(\mathbf{m}_p^r - \mathbf{I})|} \ + \ \mathcal{O}(\hbar^2) \ , \tag{27}$$

where T_p is the period of the prime periodic orbit p and $\mathbf{m}_p$ is the same matrix of the linearized Poincaré map as in Eq. (19).

The Laplace transform of this evolution operator gives the 'trace' of the resolvent of the Liouvillian operator [2]

$$\int_0^{\infty} dt \ \exp(-st) \ \mathrm{Tr}_E \ \exp(\mathcal{L}t) \ = \ \mathrm{Tr}_E \ \frac{1}{s - \mathcal{L}} \ = \ \frac{\partial}{\partial s} \ \ln \ Z_{\rm cl}(s;E) + \ \mathcal{O}(\hbar^2) \ , \tag{28}$$

in terms of the classical Zeta function

$$Z_{\rm cl}(s;E) \ = \ \prod_p \prod_{m_1,\ldots,m_{f-1}=0}^{\infty} \left\{ 1 \ - \ \frac{\exp\left[-sT_p(E)\right]}{\prod_{k=1}^{f-1} |\Lambda_p^{(k)}(E)| \Lambda_p^{(k)}(E)^{m_k}} \right\}^{(m_1+1)\cdots(m_{f-1}+1)} \ . \tag{29}$$

The zeros of this classical Zeta function, $Z_{\rm cl}(s;E) = 0$ give minus the classical decay rates for the dynamics on each energy shell $H_{\rm cl} = E$. We notice that both the periods T_p and the stability eigenvalues Λ_p depend on the energy E, as expected. At this level, we see the importance of introducing the energy superoperator and its eigenstates, which allows us to obtain a classical dynamics restricted to one energy shell as it should be. This classical behavior is in contrast with the quantum-mechanical behavior in which the quantization of energy selects the eigenenergies. In a classical scattering system, the leading Pollicott-Ruelle resonance gives the so-called classical escape rate $\gamma_{\rm cl}(E) > 0$ of trajectories out of the interacting region

$$s \ = \ s_0(E) \ = \ - \ \gamma_{\rm cl}(E) \ . \tag{30}$$

We remark that the classical Zeta function (29) has similarities with the semiclassical quantum Zeta function (23), but they have also important differences because they are concerned by the time evolution of different types of quantities. The semiclassical quantum Zeta function is concerned by quantum amplitudes while the classical Zeta function is concerned by classical probabilities. Since the probabilities are essentially given by the squares of the quantum amplitudes, we may explain the differences as follows. Let us consider the quantum amplitude associated with an unstable periodic orbit of a two-degrees-of-freedom system

$$\frac{\exp\left[\frac{i}{\hbar} S_p(E) - i\frac{\pi}{2}\mu_p\right]}{|\Lambda_p(E)|^{\frac{1}{2}}} \ . \tag{31}$$

This amplitude depends on the quantum phase of the orbit and on the square root of its stability eigenvalue. At the level of the density matrix, the relevant quantity is the amplitude (31) multiplied by the complex conjugate of another quantum amplitude, which should give a classical probability. Since we consider in Eq. (29) a time-dependent process with a decay rate $-s$, the other amplitude should be taken at the energy $E' = E - i\hbar s$ with respect to the energy

E of (31). The difference between E' and E is an imaginary energy corresponding to the imaginary frequency $-s$. Accordingly, in the classical expression, we expect to find the factor

$$
\begin{aligned}
& \frac{\exp\left[\frac{i}{\hbar}S_p(E) - i\frac{\pi}{2}\mu_p\right]}{|\Lambda_p(E)|^{\frac{1}{2}}} \; \frac{\exp\left[-\frac{i}{\hbar}S_p(E') + i\frac{\pi}{2}\mu_p\right]}{|\Lambda_p(E')|^{\frac{1}{2}}} \\
\simeq \; & \frac{\exp \frac{i}{\hbar}\left[S_p(E) - S_p(E) + i\hbar s T_p(E) + \mathcal{O}(\hbar^2)\right]}{|\Lambda_p(E)|} \\
\simeq \; & \frac{\exp\left[-sT_p(E)\right]}{|\Lambda_p(E)|} \; ,
\end{aligned}
\tag{32}
$$

because of the classical formula (21). This argument explains that:

1. The stability eigenvalues themselves appear in the classical Zeta function (29) instead of their square roots which appear in the semiclassical Zeta function (23).
2. The period multiplied by the decay rate $-s$ appears in (29) instead of the quantum phase as in (23).

A last difference comes from the exponents $(m_k + 1)$ of the periodic-orbit factors in (29), which has its origin also in the fact that the stability eigenvalues are classically involved instead of their square roots.

E. Characterization of classical chaos

Nonlinear classical systems governed by Hamilton's equations generate a dynamics of trajectories. In the phase space of the system, these trajectories may be stable or unstable. The possible dynamical instability may generate dynamical randomness. Under such circumstances, the time average of an observable may be equivalent to an average over a statistical ensemble of points which are distributed in the phase space according to an invariant probability measure.

Such invariant measures can be constructed from the knowledge of the instability of the trajectories visiting successively different cells $\omega_1\omega_2\cdots\omega_n$ in the phase space. In a two-degrees-of-freedom system, the dynamics stretches the phase-space cells by a so-called stretching factor $\Lambda_{\omega_1\cdots\omega_n}$ which corresponds to a time interval $T_{\omega_1\cdots\omega_n}$. An invariant measure can be defined by assuming that the probability weight of the trajectories visiting the cells $\omega_1\omega_2\cdots\omega_n$ is smaller if this phase-space region is more unstable. Different invariant measures can be constructed depending on an exponent β given to each stretching factor [37]. In the limit $n \to \infty$, the probability weight of the successive cells $\omega_1\omega_2\cdots\omega_n$ is thus defined by

$$
\mu_\beta(\omega_1\omega_2\cdots\omega_n) \;\simeq\; \frac{|\Lambda_{\omega_1\omega_2\cdots\omega_n}|^{-\beta}}{\sum_{\omega_1\omega_2\cdots\omega_n}|\Lambda_{\omega_1\omega_2\cdots\omega_n}|^{-\beta}} \; , \tag{33}
$$

where the denominator guarantees that the invariant measure is normalized to unity. The classical dynamics naturally induces the invariant measure with $\beta = 1$, in which case the probability weight is inversely proportional to the stretching factor. This result is consistent with the fact that each periodic orbit has a probability weight which is inversely proportional to its stability eigenvalue as seen in Eq. (32).

In analogy with equilibrium statistical mechanics, Ruelle has introduced an associated pressure function as [38]

$$
P(\beta) \;\equiv\; \lim_{\substack{t\to\infty \\ \delta\to 0}} \frac{1}{t} \ln \sum_{\substack{\omega_1\cdots\omega_n \\ t < T_{\omega_1\cdots\omega_n} < t+\Delta t}} |\Lambda_{\omega_1\omega_2\cdots\omega_n}|^{-\beta} \; , \tag{34}
$$

where δ is the diameter of the cells ω. For a two-degrees-of-freedom system, the invariant measure μ_β is equivalently characterized by the KS entropy per unit time and by the mean Lyapunov exponent, or by the pressure function.

For an open chaotic system with two degrees of freedom (2F), the dynamics may select a set of trajectories which are forever trapped in the interacting region. This set is called the repeller and it is characterized by an escape rate as well as by partial fractal dimensions. All the different characteristic quantities of the repeller can be obtained from the pressure function as shown in Table 1 [4, 6, 39, 40]. In Table 1, the four first quantities are evaluated for the natural invariant measure with $\beta = 1$ which is directly induced by the classical dynamics. The two last quantities characterize the topological chaos which is probed with the invariant measure with $\beta = 0$ for which all the trajectories have an identical probability weight.

The pressure function can be evaluated from the unstable periodic orbits of the system as the leading zero $s = P(\beta;E)$ of the following inverse Ruelle zeta function

$$\zeta_0^{-1}(s;\beta;E) \;=\; \prod_p \left\{ 1 \;-\; \frac{\exp\left[-sT_p(E)\right]}{\prod_{k=1}^{f-1} |\Lambda_p^{(k)}(E)|^{\beta}} \right\} \; . \tag{35}$$

The pressure function depends on the energy shell where the invariant measure (33) is defined.

TABLE I: Characteristic quantities of chaos in an open 2F system

Escape rate	$\gamma_{\rm cl} = -P(1)$
Lyapunov exponent	$\lambda = -P'(1)$
KS entropy	$h_{\rm KS} = \lambda - \gamma_{\rm cl} = P(1) - P'(1)$
Partial information dimension	$d_{\rm I} = \frac{h_{\rm KS}}{\lambda} = 1 - \frac{P(1)}{P'(1)}$
Topological entropy	$h_{\rm top} = P(0)$
Partial Hausdorff dimension	$P(d_{\rm H}) = 0$

III. SCATTERING THEORY OF DECAY PROCESSES

A. Scattering resonances

Decay processes occur in finite systems which are excited by collisions with particles or waves coming from the exterior of the system. This is the case for a vast set of experimental situations which can therefore be studied from the viewpoint of scattering theory.

If the Hamiltonian of the system is time independent, the time evolution of the system can always be described by the time evolution operator (2) or the propagator (3), which admit a decomposition on the eigenfunctions of the Hamiltonian. The quantum-mechanical time evolution is thus completely determined by the energy spectrum of the system.

For the purpose of obtaining the asymptotic time evolution for either $t \to \pm\infty$, a remarkable method is given by the analytic continuation of the resolvent of the Hamiltonian toward either the lower-half complex energy surface or the upper-half surface, respectively. In this way, the unitary time evolution is asymptotically approximated by either the evolution operator of the forward semigroup or the one of the backward semigroup [23]. This method is most natural and convenient to derive the asymptotic irreversible time evolution for the quantum wavefunction. By analytic continuation, we can obtain the contributions from the complex singularities of the Hamiltonian resolvent, such as the poles and the branch cuts which are issued from the energy thresholds of each scattering channel. The poles of the resolvent are located in the lower second Riemann sheet of the complex energy surface at the complex energies

$$z_r \;=\; E_r \;-\; i\,\frac{\Gamma_r}{2} \; , \tag{36}$$

and are called the scattering resonances of the system. These poles of the Hamiltonian resolvent are also poles of the S-matrix describing the scattering of plane waves in the system. If the resonance is sufficiently isolated and is excited individually, its contribution to the wavepacket decays in time with damped oscillations and the corresponding probability density decays exponentially with a lifetime given by the imaginary part of the complex energy (36) as

$$\tau_r \;=\; \hbar/\Gamma_r \; . \tag{37}$$

Long-time tails with power-law decays of the wavefunction also exist at energies near the thresholds where new scattering channels open but they play a minor role [23].

This framework of the scattering and resolvent theories provides a firm basis to study the decay properties of open few-body quantum systems. In this framework, the resonances give direct information on the decay because each of them determines a lifetime. In particular, reaction rates can be determined from the knowledge of the scattering resonances. Moreover, we can associate some Hamiltonian eigenstates with the resonances, in a similar way as eigenstates are associated with the bound states.

In many systems, the scattering resonances form a dense spectrum which has to be analyzed statistically. For this purpose, the semiclassical theory is an important method where the quantum-mechanical quantities such as the Hamiltonian resolvent or its trace are expanded around the classical trajectories in the limit $\hbar \to 0$. Whether the states are pure or mixed, different expressions are obtained in the semiclassical limit. For both pure and mixed states, the time evolution can be decomposed onto the quantum scattering resonances. However, many systems evolve in a semiclassical regime involving numerous quantum scattering resonances. The effect of the accumulation of many quantum scattering resonances can be studied with the classical Liouvillian theory. In this regard, the classical escape rate can be considered as an average over the multiple quantum decays due to the many individual quantum scattering resonances.

B. Distributions of scattering resonances and bound on the quantum lifetimes

As we have shown here above, the quantum scattering resonances are given by the poles of the resolvent of the Hamiltonian operator. In the semiclassical approximation, the periodic-orbit contributions of this resolvent are given as [23]

$$\mathrm{tr}\frac{1}{z-H}\Big|_{\mathrm{po}} = \frac{\partial}{\partial z}\ln Z(z) \; + \; \mathcal{O}(\hbar^0) \; , \tag{38}$$

in terms of the semiclassical quantum Zeta function (23) with $\lambda = 0$ for a classically hyperbolic system with unstable periodic orbits such as a classically chaotic system. As a consequence of (38), the poles of the resolvent are semiclassically obtained from the zeros of the Zeta function: $Z(z) = 0$.

For a system with two degrees of freedom, the periodic-orbit contributions to the resolvent is a series which can thus be evaluated as

$$\mathrm{tr}\; \frac{1}{z-H}\Big|_{\mathrm{po}} \sim \sum_p \sum_{r=1}^{\infty} T_p(z) \frac{\exp\left[\frac{i}{\hbar} r S_p(z) - i\frac{\pi}{2} r\mu_p\right]}{|\Lambda_p(z)|^{\frac{r}{2}}} \; . \tag{39}$$

Taking a complex energy

$$z = E - i\, \frac{\hbar}{2\tau} \; , \tag{40}$$

the reduced action can be expanded in powers of $\hbar$ as

$$S_p(z) = S_p(E) - i\, \frac{\hbar}{2\tau}\, T_p(E) + \mathcal{O}(\hbar^2) \; , \tag{41}$$

because of Eq. (21). Whereupon the series becomes

$$\mathrm{tr}\frac{1}{z-H}\Big|_{\mathrm{po}} \sim \sum_p \sum_{r=1}^{\infty} T_p(E) \; \exp\left[\frac{i}{\hbar} r S_p(E) - i\frac{\pi}{2} r\mu_p\right] \frac{\exp\left[rT_p(E)/2\tau\right]}{|\Lambda_p(E)|^{\frac{r}{2}}} \; . \tag{42}$$

This series converges absolutely under the condition that the sum of the absolute values of the terms with their period T_p in the time interval $t < T < t + \Delta t$ vanishes. An upper bound on this sum is given in terms of the pressure function by

$$\sum_{t<T<t+\Delta t} T \; \frac{\exp\left(T/2\tau\right)}{|\Lambda_T|^{\frac{1}{2}}} \; \sim_{t\to\infty} \; t \; \exp(t/2\tau) \; \exp\left[tP(\beta = 1/2; E)\right] \; \to_{t\to\infty} \; 0 \; , \tag{43}$$

with $T = rT_p$ and $\Lambda_T = \Lambda_p^r$. We find the pressure function evaluated at $\beta = 1/2$ because the quantum amplitudes are essentially the square roots of the classical probabilities except for a quantum phase, which is not relevant for absolute convergence. We infer from (43) that the sum vanishes and the series converges absolutely under the condition that the imaginary part of the complex energy (40) satisfies $(1/2\tau) + P(1/2; E) < 0$ at the real energy E. Therefore, the poles of the resolvent may only appear at the complex energies (36) such that

$$\frac{\Gamma_r}{\hbar} \; = \; \frac{1}{\tau_r} \; \geq \; - \; 2 \; P\left(\frac{1}{2}; E_r\right) \; , \tag{44}$$

in the asymptotic limit $\hbar \to 0$ [13, 23, 32].

In this way, we observe that the pressure at $\beta = 1/2$ determines a boundary on the complex energy surface above which no resonance is expected. As long as the pressure at $\beta = 1/2$ is positive, this inequality does not impose a bound on the resonances. However, the inequality becomes effective when the pressure is negative. In this case, there is a gap below the real energy axis which is empty of scattering resonance. Since the pressure function vanishes at the partial Hausdorff dimension of the repeller in a two-degrees-of-freedom system, this gap appears when the corresponding classical dynamics has an invariant measure supported by a fractal set with a partial dimension less than one half. If $d_{\rm H} < 1/2$, we may speak about a filamentary fractal as opposed to a bulky fractal with $d_{\rm H} > 1/2$.

The above result is remarkable in many respects if we compare with the mean lifetime expected from the classical Liouvillian dynamics. Besides the bound (44), the semiclassical quantum lifetimes can also be estimated with the escape rate given by the quasiclassical Liouvillian theory. Since the classical escape rate is given by minus the pressure function at $\beta = 1$, we find that, quasiclassically, the lifetime is estimated as

$$\gamma_{\rm cl} \;=\; \frac{1}{\tau_{\rm cl}} \;=\; -\,P(1;E)\;, \tag{45}$$

instead of (44). The properties of the pressure function imply that

$$P\left(\frac{1}{2};E\right) \;\geq\; \frac{1}{2}\,P(1;E)\;. \tag{46}$$

The equality occurs if the pressure function is linear, i.e., if the scattering system has a periodic unstable motion on its repeller. If the motion on the repeller is chaotic, the pressure function is convex and a strict inequality occurs in Eq. (46). In this chaotic case, the mean classical lifetime will thus be shorter than the largest possible quantum lifetimes which may approach the semiclassical bound (44). Consequently, we find this important difference between the classically periodic and chaotic systems [13]:

$$\text{periodic}: \qquad \tau_{\rm cl}(E) \;=\; \tau_{\rm q}(E)\;, \tag{47}$$

$$\text{chaotic}: \qquad \tau_{\rm cl}(E) \;<\; \tau_{\rm q}(E)\;, \tag{48}$$

where the quantum lifetime at energy E is defined as the longest possible lifetime of the quantum scattering resonances: $\tau_{\rm q}(E) = \max\{\tau_r\}_{E_r \simeq E}$. On the other hand, the classical lifetime is defined on the decay of a quantum statistical mixture involving many individual quantum resonances, as explained in Subsection 2.4. In this sense and as suggested by comparing Eq. (45) with Eq. (44), the inverse of the classical lifetime gives some kind of average value for the imaginary parts of the energies of the quantum scattering resonances. The classical lifetime acquires its importance in the case of bulky fractal repellers, for which the bound (44) is no longer directly useful. In the case of a bulky repeller, the classical lifetime may give in some systems an estimation of the imaginary part of the energy of a typical scattering resonance.

C. Application to disk scatterers and unimolecular reactions

The resonance spectrum has been studied in detail for the scattering of a wave on several disks with different boundary conditions [30, 41, 42]. These scattering systems have also been the object of scattering experiments with acoustic waves [42] and electromagnetic microwaves [43].

The scattering resonances can also be used to characterize unimolecular reactions of molecules excited by absorption of a photon. This excitation may bring the molecule up to an upper electronic Born-Oppenheimer potential energy surface where the motion may be dissociative with a filamentary classical repeller. This is the case in $\mathrm{HgI_2}$ and $\mathrm{CO_2}$ [17], for which agreement has been found with the bound on the quantum lifetimes described here above [32].

In many molecules, the classical repeller is bulky and it traps the trajectories in a quasibounded phase-space region before escaping above a barrier which forms a bottleneck. In this bulky case, the classical escape rate becomes very useful to evaluate the unimolecular reaction rate by assuming a quasi-equilibrium in the quasibounded region. Indeed, if the repeller is bulky, the fractal dimension of the invariant measure is close to the phase-space dimension and it is reasonable to assume a quasi-equilibrium distribution in the quasibounded region. Under these assumptions of RRKM theory, the reaction rate can be calculated which gives an expression for the classical escape rate [44]. In the simplest model, the scattering resonances are supposed to be distributed around the classical escape rate according to the χ^2-distribution. This statistical theory has been applied to many experimental and numerical data on unimolecular reactions as well as to nuclear reactions.

D. Application to spatially extended scatterers

Landauer's model of electronic conductance is based on the idea that the electron undergoes a scattering process inside the electronic circuit connected to external reservoirs by wires which behave as waveguides. The circuit may be localized like for a quantum constriction but it may also be spatially extended if it is a regular or a disordered chain composed of many successive units.

Recently, we have analyzed the spectrum of resonances for the scattering of a particle in a one-dimensional potential formed by many identical units [45]. We have shown that the resonances form band structures which are reminiscent of the Bloch energy bands of the infinite periodic potential. Actually, if the potential contains N units satisfying certain conditions of regularity, $(N-1)$ resonances accumulate just below each energy band.

If the one-dimensional chain is disordered, the Anderson localization is known to happen for the infinite system. For a finite disordered chain, the spectrum of resonances and of bound states is irregular [46]. For energies where the localization length is smaller than the total length of the scatterer, the transmission coefficient vanishes and the scattering resonances have long lifetimes. At higher energies where the localization length is larger than the system size, the transmission coefficient fluctuates just below the value unity and the lifetimes of the scattering resonances are consistently much shorter [46].

In spatially extended systems with a chaotic classical dynamics, diffusion may occur as in the Lorentz gas or in the multibaker map. In such systems, the classical escape rate decreases as $\gamma_{\rm cl}(E) \simeq D(E)(\pi/L)^2$ with the system size L, where $D(E)$ is the energy-dependent diffusion coefficient [13]. A similar behavior is expected for the distribution of the imaginary parts of the quantum scattering resonances in such systems. In this context, the Pollicott-Ruelle resonances and the escape rate have been shown to play an important role in the semiclassical quantum theory of diffusion [47].

IV. MANY-BODY QUANTUM SYSTEMS

A. Transport in many-body quantum systems

Transport properties such as diffusion, viscosity, heat or electric conductivities can be described quantitatively within the Green-Kubo theory. For a quantum system in a thermal state, a transport coefficient is given by the integral of the time autocorrelation function of the microscopic current associated with the transport process according to the Kubo formula [48], which can be transformed into an Einstein-type formula by introducing the associated Helfand moment [49]. In this way, a simple proof can be given that the transport coefficient are non-negative [50].

If the many-body system is bounded, its energy spectrum is discrete and, as a consequence, its time correlation functions are almost-periodic functions of time. Such an almost-periodic function of time has the property to be recurrent, which is problematic because the recurrences spoil the Kubo formula. The way out of this difficulty is to take a thermodynamic limit where the number of particles in the system increases with the volume of the system, keeping the density constant. In this limit, the time correlation function is expected to converge to a function which decays. Indeed, for a finite system, the almost-periodic oscillations and the recurrences only appear for times longer than the Heisenberg time defined by the Planck constant multiplied by the mean level density $d_{\rm av}(E)$

$$t_{\rm Heisenberg} \;\equiv\; \hbar \; d_{\rm av}(E) \;\sim\; (\hbar/k_{\rm B}T) \; (n \; \lambda^3_{\rm de\ Broglie})^{-N} \; , \tag{49}$$

where $\lambda_{\rm de\ Broglie} \equiv 2\pi\hbar/\sqrt{mk_{\rm B}T}$ is the thermal de Broglie wavelength of the particles of mass m and n is the number of particles per unit volume. The Heisenberg time grows exponentially with the number N of particles in the system, under the condition that the temperature is large enough with respect to the particle density in order that $n \; \lambda^3_{\rm de\ Broglie} < 1$. Since the Heisenberg time becomes astronomical even for a few thousands particles under standard conditions, the Kubo formula can be justified thanks to a rapidly attained thermodynamic limit.

B. Spectral randomness in many-body quantum systems

In spite of the fact that for many-body systems the energy eigenvalues become too dense to be resolved, their spectral properties still govern the time evolution, which has motivated the statistical analysis of the energy spectrum.

A property of interest is the degeneracy of the eigenvalues, which determines the dimension of the nullspace of the quantum Liouvillian operator and, therefore, the number of constants of motion, i.e., of operator which commute with the Hamiltonian. The larger is the nullspace dimension, the greater is the number of constants of motion which may restrict the normal transport properties.

In this context, we have compared the spectral properties of different systems with many spins $S = 1/2$ forming a square two-dimensional lattice, namely, the Ising, the Heisenberg and the dipolar spin systems. This comparison has revealed strikingly different spectral properties [20].

In the Ising system, the degeneracy is the highest as expected for this exactly solvable system.

For the Heisenberg system, the degeneracy is intermediate with high degeneracies for the states associated with the ferromagnetic spin waves. Geometric and some dynamic symmetries could be used to block-diagonalize the Hamiltonian. Within the remaining blocks of the Hamiltonian, the eigenvalues follow a Poisson-type spacing statistics, suggesting the existence of further symmetries besides the one considered.

However, for the dipolar spin system, the degeneracy was the smallest due only to the known geometric symmetries. After block-diagonalization, the eigenvalues of each remaining block follow a Wigner-type spacing statistics, precluding the existence of further symmetries. The results show that the dipolar system has the less regular dynamics. The transport of heat has also been studied numerically [52].

The statistics of the curvature of the energy levels, i.e. of the second derivative of each eigenvalue with respect to an external field, has also been studied for the dipolar spin system [51]. The probability density of the level curvatures presents the universal power law $\mathcal{P}(K) \sim K^{-3}$ for $K \to \infty$, confirming the existence of a Wigner spacing statistics in the dipolar spin system. The curvature distribution has also been considered in the context of electronic states in disordered media in relation to the problem of electronic conductance [53].

C. nonMarkovian stochastic Schrödinger equation for a slow subsystem coupled to a fast bath

Among the possible many-body quantum systems, we often find a small and slow subsystem which interacts with a fast thermal bath. Examples of such systems are a spin or a cluster of spins coupled to the vibrations of their host molecule, liquid or solid, which is common in NMR. Effective two-level subsystems also occur in electron- or charge-transfer reactions in condensed phases. The total Hamiltonian of such systems has the form

$$H \;=\; H_{\rm s} \;+\; H_{\rm b} \;+\; \lambda\, V \qquad \text{with} \qquad V \;=\; \sum_{\alpha} S_\alpha\; B_\alpha \;, \tag{50}$$

where $H_{\rm s}$ is the Hamiltonian of the isolated subsystem, $H_{\rm b}$ is the one of the bath, while the interaction between the subsystem and the bath is described by the subsystem operators S_α and the bath operators B_α, respectively.

The kinetics of such open systems may be described by a quantum master equation which governs the time evolution of the subsystem density matrix [54]. If we make a formal analogy with a classical process such as Brownian motion, the master equation would be the Fokker-Planck equation but we should also expect the existence of an equivalent stochastic equation such as the Langevin stochastic differential equation. Its quantum analogue would be a stochastic Schrödinger equation, as recently introduced and studied [55, 56]. However, the recently introduced stochastic Schrödinger equations are restricted to be equivalent to Markovian quantum master equations of Lindblad type [57]. The Markovian assumption requires that the time correlation functions of the bath

$$C_{\alpha\beta}(t) \;=\; \langle B_\alpha(t) B_\beta(0)\rangle \;, \tag{51}$$

be proportional to the delta Dirac distribution $\delta(t)$, which is a good approximation for light-matter interaction because of the fast velocity of light.

However, most of the thermal baths have a nonvanishing relaxation time for their time correlation functions. For such systems, we have recently derived a nonMarkovian stochastic Schrödinger equation in the weak coupling limit [22]. The derivation is based on three main ideas:

1. A suitable definition is given to the concept of ‘wavefunction’ for a subsystem. The stochastic Schrödinger equation is supposed to govern the time evolution of such a ‘subsystem wavefunction’. For this purpose, the total wavefunction is decomposed in the basis of the eigenfunctions $\{\chi_n(x_{\rm b})\}$ of the bath Hamiltonian:

$$\Psi(x_{\rm s}, x_{\rm b}; t) \;=\; \sum_n \;\phi_n(x_{\rm s}; t)\;\chi_n(x_{\rm b}) \;. \tag{52}$$

The coefficients $\phi_n(x_{\rm s}; t)$ of this linear decomposition still depend on the subsystem coordinates $x_{\rm s}$ and they play the role of the ‘subsystem wavefunctions’. Since the bath is very large, there is an enormous number of such coefficients $\phi_n(x_{\rm s}; t)$, many of them behaving statistically in a similar way. Accordingly, we suppose here that they form a statistical ensemble. One typical coefficient may be expected to evolve stochastically because it is driven by all the other coefficients.

2. In order to obtain the equation of motion for the ‘typical’ coefficient $\phi_l(x_{\rm s}; t)$, we use the Feshbach projection-operator method. This projection method is used in the Hilbert space, which fulfils our need to remain with a

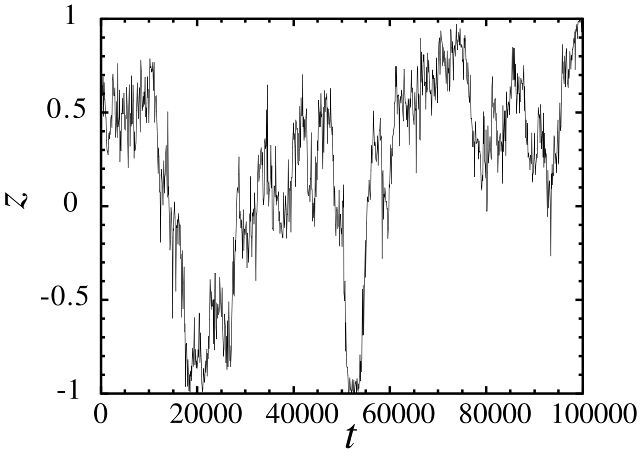

FIG. 1: Bloch component $z = \langle \sigma_z \rangle$ versus the time t for an individual trajectory of the nonMarkovian stochastic Schrödinger equation for the spin-boson model.

quantum-state description. An operator P of projection onto the 'typical' coefficient $\phi_l(x_{\rm s};t)$ as well as its complement $Q = I - P$ are introduced by

$$(P\ \Psi)(x_{\rm s}, x_{\rm b}) \equiv \phi_l(x_{\rm s})\ \chi_l(x_{\rm b})\ , \tag{53}$$

$$(Q\ \Psi)(x_{\rm s}, x_{\rm b}) \equiv \sum_{n\,(\neq l)} \phi_n(x_{\rm s})\ \chi_n(x_{\rm b})\ , \tag{54}$$

which obey the standard relations for projector operators: $P^2 = P$, $Q^2 = Q$, and $QP = PQ = 0$. Using the projection method by Feshbach, the equation for the typical coefficient $P\Psi(t)$ is obtained as

$$\begin{aligned} i\ \partial_t\ P\Psi(t) &= PHP\ P\Psi(t)\ +\ PHQ\ e^{-iQHQt}\ Q\Psi(0) \\ &-\ i \int_0^t d\tau\ PHQ\ e^{iQHQ(\tau-t)}\ QHP\ P\Psi(\tau)\ . \end{aligned} \tag{55}$$

In the right-hand side, the first term is eseentially the subsystem Hamiltonian, the second is the stochastic forcing of the subsystem by the thermal bath and the third is the dissipative loss from the subsystem toward the bath.

3. In order to close the equation for the typical coefficient $P\Psi(t)$ or $\phi_l(x_{\rm s};t)$, a triple hypothesis is introduced. Firstly, the average over a typical bath eigenfunction $\chi_l(x_{\rm b})$ is assumed to be equivalent to an average over a thermal statistical mixture for the bath. Secondly, the different subsystem wavefunctions $\phi_m(x_{\rm s};t)$ are assumed to differ by a random phase. Thirdly, the noises are assumed to be Gaussian. The first part of the hypothesis can be justified if the bath is classically chaotic and has eigenfunctions $\chi_n(x_{\rm b})$ which satisfy the Berry-Voros conjecture [25]. In this regard, Srednicki has shown that the quantum thermal equilibrium distributions for Bosons and Fermions are consequences of the Berry-Voros conjecture [21]. The second part of the hypothesis allows us to fix the form of the initial wavefunction.

By using this triple hypothesis as well as a perturbative expansion up to second order in the coupling parameter λ, we have been able [22] to derive the following nonMarkovian stochastic Schrödinger equation for a wavefunction $\psi(x_{\rm s};t)$ which is proportional to a typical coefficient $\phi_l(x_{\rm s};t)$ of the decomposition (52):

$$\begin{aligned} i\ \partial_t\ \psi(t) &= H_{\rm s}\ \psi(t)\ +\ \lambda \sum_\alpha \eta_\alpha(t)\ S_\alpha\ \psi(t) \qquad (56) \\ &-\ i\ \lambda^2 \int_0^t d\tau \sum_{\alpha\beta} C_{\alpha\beta}(\tau)\ S_\alpha\ e^{-iH_{\rm s}\tau}\ S_\beta\ \psi(t-\tau)\ +\ \mathcal{O}(\lambda^3)\ , \end{aligned}$$

where $C_{\alpha\beta}(t)$ are the bath correlation functions (51) and $\eta_\alpha(t)$ are Gaussian noises $\eta_\alpha(t)$ satisfying

$$\overline{\eta_\alpha(t)} = 0\ , \qquad \overline{\eta_\alpha(t)\eta_\beta(0)} = 0\ , \qquad \text{and} \qquad \overline{\eta^*_\alpha(t)\eta_\beta(0)} = C_{\alpha\beta}(t)\ . \tag{57}$$

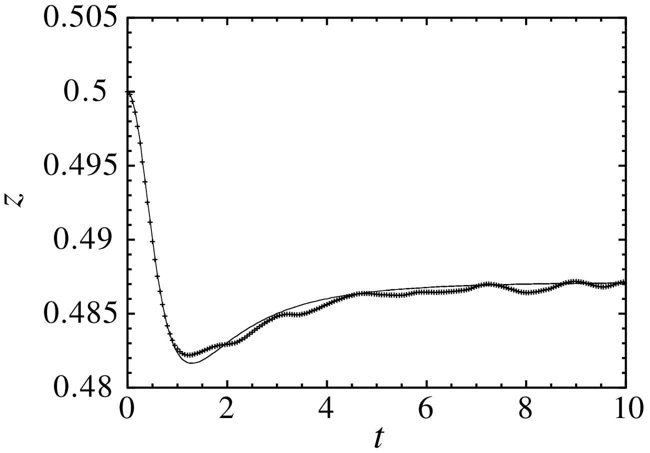

FIG. 2: For the spin-boson model under the same conditions as in Fig. 1, comparison between a simulation using the nonMarkovian stochastic Schrödinger equation (56) and the prediction of the corresponding nonMarkovian master equation at the early stage of the time evolution of the Bloch variable z in order to show the slippage of initial conditions over the bath relaxation time $t_{\rm b} \sim 1$. The average (pluses) is here taken over a statistical ensemble of 2×10^5 individual trajectories.

We have shown that this stochastic equation has for master equation the nonMarkovian quantum master equation of second-order perturbation theory [22]. In the long-time limit, this nonMarkovian master equation tends to the famous Redfield master equation [54] supplemented by a slippage of initial conditions [58]. This slippage of initial conditions can solve the well-known problem of the violation of positivity by the Redfield master equation [58]. The nonMarkovian stochastic Schrödinger equation also avoids this problem of positivity and consistently reproduces the slippage of initial conditions [22].

Our stochastic Schrödinger equation has been applied to the spin-boson model of a spin $S = 1/2$ coupled to a thermal bath of bosonic harmonic oscillators. Fig. 1 depicts the spin variable $z = \langle\sigma_z\rangle$ for a long trajectory of an individual system taken in the statistical ensemble. Fig. 2 shows an average over the statistical ensemble and the agreement between the simultation with our stochastic Schrödinger equation and the calculation based on the quantum master equation just after the initial condition, demonstrating the slippage of initial conditions on the time scale of relaxation of the bath correlation function (51).

D. Quantum entropies per unit time and the characterization of dynamical randomness

Stochastic behavior is expected to occur in large many-body quantum systems. In contrast, few-body quantum systems which are bounded have a discrete energy spectrum and, therefore, an almost-periodic time evolution. In the thermodynamic limit, the almost-periodic time evolution could be expected to become stochastic because the spectrum of the time evolution operator typically becomes continuous in this limit. Such a stochasticity is also the feature of classical chaotic dynamical systems where dynamical entropies per unit time have been defined in order to characterize the dynamical randomness.

In the late fifties, Kolmogorov and Sinai have rigorously defined an entropy per unit time as follows. For classical dynamical systems, suppose that the dynamics is a flow $\mathbf{\Phi}^t$ acting in the phase space Γ of the system and which maps the initial conditions $\mathbf{X}_0$ onto the current point $\mathbf{X}_t = \mathbf{\Phi}^t\mathbf{X}_0$. The dynamics is supposed to leave invariant a probability measure μ. The classical observables are the functions defined in the phase space and they form a commutative algebra in which the flow induces the time evolution

$$\phi^t\left[A(\mathbf{X})\right] \;=\; A(\mathbf{\Phi}^t\mathbf{X}) \; . \tag{58}$$

Among the observables, we find the indicator functions of cells ω defined in the phase space: $A(\mathbf{X}) = I_\omega(\mathbf{X})$. We define a denumerable partition $\mathcal{P} = \{\omega\}$ of the phase space Γ into non-overlapping cells covering the whole phase space: $\omega \cap \omega' = \emptyset$ and $\cup\omega = \Gamma$. The classical system is observed stroboscopically at regular time intervals $t_n = n\Delta t$ with $n = 0, 1, 2, ...$ The probability that the trajectories visit successively the cells $\omega_0\omega_1\omega_2\cdots\omega_{n-1}$ at the times

$t_0, t_1, t_2, ..., t_{n-1}$ is $\mu(\omega_0\omega_1\omega_2\cdots\omega_{n-1})$. The entropy per unit time of the partition $\mathcal{P}$ is defined by

$$h(\mathcal{P}) \equiv \lim_{t\to\infty} -\frac{1}{n\Delta t} \sum_{\omega_0\omega_1\cdots\omega_{n-1}} \mu(\omega_0\omega_1\cdots\omega_{n-1}) \ln\mu(\omega_0\omega_1\cdots\omega_{n-1}) \ . \tag{59}$$

The KS entropy per unit time is the supremum of the entropy over all the partitions [59]

$$h_{\rm KS} = \sup_{\mathcal{P}} h(\mathcal{P}) \ . \tag{60}$$

The entropy per unit time is the rate of decrease of the multiple-time probabilities because we have the

Shannon-McMillan-Breiman theorem: If $(\mathbf{\Phi}^t, \Gamma, \mu)$ is an ergodic classical dynamical system and $\mathcal{P}$ is a partition of Γ, then

$$\mu(\omega_0\omega_1\cdots\omega_{n-1}) \sim \exp\left[-n \ \Delta t \ h(\mathcal{P})\right] \ , \tag{61}$$

for almost all initial conditions $\mathbf{X}\in\Gamma$ such that $\mathbf{\Phi}^{k\Delta t}\mathbf{X}\in\omega_k$ [59].

We observe that the entropy per unit time is a property of n-time probabilities, i.e., of n-time correlation function, in contrast to the transport, Burnett and super-Burnett coefficients which are properties of the 2-, 3- and 4-time correlation functions. This observation gives us a hint about how the concept of KS entropy can be generalized to quantum systems.

In 1987, Connes, Narnhofer and Thirring (CNT) made a first proposal for an extension of the concept of dynamical entropy to noncommutative algebras [60]. The CNT quantum entropy reduces to the KS entropy when the algebra of operators becomes commutative. The notion of partition was replaced by a set of noncommutative subalgebras and the entropy was defined for this set of subalgebras. The CNT quantum entropy per unit time was defined by considering the subalgebras generated by shifting successively in time an initial subalgebra. The CNT entropy per unit time vanishes as expected for few-body quantum systems with a discrete energy spectrum. It may be positive for large quantum systems with infinitely many particles in a thermal state. For noninteracting Bosons or Fermions, a closed expression was derived for the CNT entropy per unit time [61]. As expected again by correspondence with the classical entropy, this entropy per unit time is proportional to the surface crossed by the ideal gas of Bosons or Fermions. The corresponding classical entropy per unit time of an ideal gas is recovered in the limit $\hbar\to 0$, as shown elsewhere [62].

More recently, another definition of a quantum entropy per unit time was proposed by Alicki and Fannes [63]. It is based on a decomposition $\mathcal{X}$ of the identity operator as

$$\sum_\omega X_\omega^\dagger \ X_\omega = I \ , \tag{62}$$

where X_ω are operators in the quantum algebra. These operators are shifted in time by steps Δt according to

$$\phi^t(X_\omega) = X_\omega(t) = \exp(iHt/\hbar) \ X_\omega \ \exp(-iHt/\hbar) \ . \tag{63}$$

A multiple-time matrix D_n of time correlation functions is defined by the matrix elements

$$\begin{aligned} D_n\left[\Omega,\Omega'\right] \equiv \ & {\rm tr}\Big[\underbrace{X_{\omega_{n-1}}(t_{n-1})\cdots X_{\omega_1}(t_1)X_{\omega_0}(t_0)}_{\Omega} \\ & \times\rho_{\rm eq}\underbrace{X^\dagger_{\omega'_0}(t_0)X^\dagger_{\omega'_1}(t_1)\cdots X^\dagger_{\omega'_{n-1}}(t_{n-1})}_{\Omega'}\Big] \ , \end{aligned} \tag{64}$$

where $\Omega=\omega_0\omega_1\cdots\omega_{n-1}$ and $\Omega'=\omega'_0\omega'_1\cdots\omega'_{n-1}$ are two arbitrary sequences of labels of the operators X_ω and where $\rho_{\rm eq}$ is the equilibrium density matrix. If there are M operators X_ω in the decomposition (62), the matrix (64) has the size $M^n\times M^n$. This matrix is Hermitian $D_n[\Omega,\Omega'] = D_n[\Omega',\Omega]^*$ and non-negative.

An example of decomposition is given by taking the operators X_ω as the projection operators P_ω, which satisfy (62) because $P_\omega P_{\omega'} = P_\omega\delta_{\omega\omega'}$, $P_\omega = P_\omega^\dagger$, and $\sum_\omega P_\omega = I$. With this assumption, the sequences Ω and Ω' define two quantum histories of Griffiths, Gell-Mann, Hartle and Omnès and the matrix (64) characterizes the decoherence between the quantum histories Ω and Ω' [64]. In particular, each diagonal element of the decoherence matrix is non-negative, $D_n[\Omega,\Omega]\geq 0$, and defines a probability for the quantum history Ω. If the histories Ω and Ω' have no common coherence the matrix element $D_n[\Omega,\Omega']$ vanishes.

If the algebra is commutative as in classical mechanics, the projection operators P_ω may be taken as the indicator functions $I_\omega(\mathbf{X})$ of the cells of a partition $\mathcal{P} = \{\omega\}$ of the classical phase space. In this case, the different factors composing (64) commute and $D_n[\Omega, \Omega'] = 0$ if $\Omega \neq \Omega'$ because the cells of the partition do not overlap. Therefore, the decoherence matrix is diagonal for a commutative algebra as in classical dynamical systems

$$\text{commutative algebra:} \qquad D_n[\Omega, \Omega'] \; = \; D_n[\Omega, \Omega] \; \delta_{\Omega\Omega'} \; . \tag{65}$$

The Alicki-Fannes (AF) entropy per unit time of a quantum dynamical system is defined by [63]

$$h_{\rm AF} \;\equiv\; \sup_{\mathcal{X}} \lim_{n\to\infty} \; - \frac{1}{n\Delta t} \; {\rm Tr} \; \mathsf{D}_n \ln \mathsf{D}_n \; . \tag{66}$$

For a commutative algebra, the AF entropy reduces to the KS entropy by the property (65).

A Renyi-type quantum entropy per unit time can similarly be defined as

$$h(q) \;\equiv\; \sup_{\mathcal{X}} \lim_{n\to\infty} \; - \frac{1}{n\Delta t} \; \frac{\ln {\rm Tr} \; \mathsf{D}_n^q}{q-1} \; , \tag{67}$$

with a Renyi parameter q. For $q = 1$, $h(q) = h_{\rm AF}$. The quantum entropy (67) reduces to the classical Renyi-type entropy per unit time in the classical limit $\hbar \to 0$ by (65).

The above entropies per unit time are expected to be nonvanishing only for infinite quantum systems defined by a thermodynamic limit. We may conjecture that, for a quantum system with a positive entropy per unit time, a matrix element of (64) would decay exponentially in a similar way as predicted by the classical Shannon-McMillan-Breiman theorem (61). Already the diagonal matrix elements of (64) have been shown to decay exponentially for the system of quantum spins coupled by a dipolar interaction [65].

The AF entropy has already been evaluated numerically for finite quantum systems confirming the vanishing of the entropy per unit time in these systems. Many questions remain open concerning its value in infinite quantum systems where it is conjectured to be positive.

V. CONCLUSIONS AND PERSPECTIVES

We have given a general overview of recent results on the decay, transport and stochastic properties of quantum systems.

In Section 2, we have described the quasiclassical (Liouvillian) and the periodic-orbit semiclassical approaches to quantum systems. We have shown that, generally, a spectral function can be decomposed into a quasiclassical smooth contribution plus semiclassical periodic-orbit contributions which oscillate with the frequency or the energy and which are supposed to approximate the effect of quantization of energy. The smooth quasiclassical contribution is obtained in the Wigner representation by a Weyl series in powers of the Planck constant. The leading term is the classical expression. The semiclassical periodic-orbit contributions are of Gutzwiller-type and their precise form depends on the stability of the periodic orbits. Unstable periodic orbits only contribute by terms of order $\hbar^{-1}$ while the leading classical term is of order $\hbar^{-f}$ where f is the number of degrees of freedom. This result is of special importance in our context because it shows that the periodic-orbit contributions will in general become negligible in many-body quantum systems with $f \to \infty$. Therefore, we may conclude that the Weyl series would give the essential contribution in interacting many-body quantum systems at nonvanishing temperatures such as fluids. The periodic-orbit contributions are nevertheless important in microscopic and mesoscopic quantum systems like atoms, nuclei, molecules, atomic clusters, or in solid-state systems where the quantum coherence of the few-body dynamics remains important.

The contributions of the unstable periodic orbits can be expressed as the logarithmic derivative of a semiclassical quantum Zeta function which is a product over all the periodic orbits. This result appears to be general in the Gutzwiller semiclassical theory which is based on the periodic-orbit trace formula. In this regard, it should be emphasized that the periodic orbits are selected in the semiclassical approximation because the quantum expression is defined by the trace of an operator involving an evolution operator or a resolvent operator. The trace is given by a Feynman path integral where the paths are closed on themselves so that, in the semiclassical limit, the paths reduce to closed classical trajectories, i.e., to periodic orbits (and also to stationary points).

Furthermore, we have pointed out that different expressions are obtained for the spectral function whether it is defined by an average over a pure or a mixed state. In the case of a pure state, the leading quasiclassical term is a microcanonical average of a static quantity involving the pure state and the operator of the spectral function. In the case of a mixed state, the leading quasiclassical term is the Fourier transform of the classical autocorrelation function. The decay of such classical autocorrelation functions is often controlled by classical resonances called the

Pollicott-Ruelle resonances which can be calculated thanks to a classical trace formula derived by Cvitanović and Eckhardt [36]. This classical trace formula is essentially the trace of the resolvent of the classical Liouvillian operator and, for a chaotic system, it is given by the logarithmic derivative of a classical Zeta function which is also a product over the unstable periodic orbits of the system. The differences and similarities between the semiclassical quantum Zeta function and the classical Zeta function have been explained in Subsection 2.4. The large-deviation formalism to characterize classical chaos was also summarized in Subsection 2.5.

In Section 3, the semiclassical methods have been applied to quantum scattering systems in order to characterize the decay processes which usually take place in scattering systems. The decay can be described thanks to the quantum scattering resonances which are the poles of the scattering matrix or also the poles of the resolvent of the Hamiltonian operator. This approach is of prime importance, in particular, in chemical kinetics in order to study unimolecular reactions.

The semiclassical approach becomes of interest in systems where the scattering resonances accumulate and where the resonance spectrum needs to be characterized by its statistical properties. The periodic-orbit semiclassical method turns out to be powerful in this context to describe the structure of the resonances spectrum at high energies where the scattering resonances can be approximated by the zeros of the semiclassical quantum Zeta function.

Moreover, a bound on the quantum lifetimes can be obtained which is useful when the classical repeller, made of trajectories trapped in the interacting region, is filamentary. On the other hand, we have shown that a decay process involving many scattering resonances may behave quasiclassically and obey the Liouvillian dynamics. In this case, the Pollicott-Ruelle resonances become relevant and, in particular, the leading resonance which is the classical escape rate. In this regard, the classical escape rate appears as a kind of average over the many quantum rates defined by the individual scattering resonances. For classically chaotic systems, we have shown that the classical lifetime corresponding to the escape rate is shorter than the longest quantum lifetimes. This result is compatible with the interpretation of the classical escape rate as an average over the quantum rates associated with the scattering resonances. The classical behavior predicted by the escape rate is thus expected to occur on an intermediate time scale, after which the quantum scattering resonances with the longest lifetimes would dominate the decay process. The theory is illustrated by applications to the disk scatterers, to ultrafast unimolecular reactions, and also to spatially extended scatterers.

In Section 4, we have been concerned by systems with many degrees of freedom taken in the thermodynamic limit. It is in this limit that the time evolution of a bounded quantum system may have a continuous spectrum and, thus, become mixing. The mixing property is indeed required in order to guarantee the relaxation of the time correlation functions and is, therefore, a necessary condition for the existence of positive and finite transport coefficients according to the Green-Kubo formula, as explained in Subsection 4.1.

In Subsection 4.2, we have presented several spectral properties of systems of increasing size in the case of spin systems. In particular, the number of constants of motion has been studied as well as the Wigner spacing statistics [20]. Different spectral statistics are observed for systems with or without dynamical constants of motion, which are expected to determine the transport properties of the infinite system. Here, the observation of a Wigner statistics is evidence for the absence of extra constants of motion. Similar results have been obtained for electronic systems. Such properties of spectral statistics are thus expected to be general and of importance for many-body quantum systems.

Subsection 4.3 contains a summary of a recent derivation of a nonMarkovian stochastic Schrödinger equation, which describes the dynamics of a slow quantum subsystem interacting with a faster thermal bath [22]. This stochastic Schrödinger equation is associated with the Redfield quantum master equation with a slippage of initial conditions [58] and is thus relevant for the relaxation of spins or other two-level systems in condensed phases as in NMR. This stochastic Schrödinger equation may turn out to be useful for the simulation of quantum subsystems with a large state space of dimension $N \gg 1$, because the stochastic equation only requires to integrate the $2N$ real components of the quantum state, while the associated master equation requires the simultaneous integration of the N^2 variables of the density matrix.

Finally, in Subsection 4.4, we have presented methods to characterize dynamical randomness, i.e., stochasticity, in large quantum systems. We have argued that such a characterization can be performed with quantum entropies per unit time which are the Connes-Narnhofer-Thirring entropy and the Alicki-Fannes entropy. This later entropy can be interpreted as the rate of decay of the multiple-time decoherence matrices of the quantum histories introduced by Griffiths, Gell-Mann, Hartle, and Omnès. We should notice that we are here concerned by the decay of the decoherence matrices as the number of times increases. In a certain sense, these multiple-time decoherence matrices form the quantum generalization of the multiple-time probabilities introduced by Onsager and Machlup for classical Gaussian irreversible processes [66]. However, methods to evaluate conveniently the quantum dynamical entropy are still missing. Such methods are desirable, especially, in order to calculate the quantum corrections to the KS entropy recently obtained by kinetic theory for the hard-sphere gas [11].

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