The influence of quantization on the onset of chaos in Hamiltonian systems: The Kolmogorov entropy interpretation

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An extension of the concept of Kolmogorov entropy to quantum mechanical systems is given. Using the Kolmogorov entropy as a common basis for discussion, the onset of chaotic motion in classical mechanical and quantum mechanical systems is compared. It is found that if the spectrum of the system is discrete, the Kolmogorov entropy is zero, and therefore that a bounded quantum mechanical system cannot have chaotic motion like that observed for a corresponding classical mechanical system. This analysis leads to the prediction that if the distributions of states are similar for two bounded systems which in the classical limit have, respectively, quasiperiodic and chaotic motion, wave packets for the two systems decay at similar rates as found by Brumer and Shapiro. The relationship between the defined Kolmogorov entropy, previous interpretations of "KAMlike" onset of chaos in quantum mechanical systems, and the role played by preparation and observation of a system in influencing the intramolecular dynamics, are discussed.

I. INTRODUCTION

The formal basis for understanding the nature of mixing and ergodic motion in a system evolving under a classical mechanical Hamiltonian has developed rapidly in the last two decades.[1,2] On the other hand, the basis for understanding the corresponding behavior in a system evolving under a quantum mechanical Hamiltonian is primitive. This paper is concerned with extension of the definition of Kolmogorov entropy to apply to quantum mechanical systems, and the consequences of that extension for the interpretation of mixing and ergodicity in any system with a discrete eigenvalue spectrum.

We begin our discussion with a summary of some of the characteristics of motion in a classical mechanical system. In particular, we note that (i) when the equation of motion is separable, the trajectories are quasiperiodic and are restricted to lie on a torus in the phase space of the system; when the equation of motion is not separable some of the trajectories are quasiperiodic, but not all; these other trajectories are not restricted to lie on a torus although they, of course, do lie on the energy surface[1-3]; (ii) the Kolmogorov–Arnold–Moser (KAM) theorem establishes that most of the quasiperiodic trajectories of some unperturbed system survive under sufficiently small perturbation, but there is also generated a set of chaotic trajectories. The relative weight of the chaotic trajectories grows as the energy increases, and they eventually fill all of the accessible phase space[4]; (iii) the onset of chaotic behavior is relatively sharp, but continuous, at an energy E_c. Below E_c almost all trajectories are quasiperiodic, but there are some chaotic trajectories. Above E_c most trajectories are chaotic, but there is also a dense set of quasiperiodic trajectories. The quasiperiodic trajectories embedded in the chaotic domain above E_c do not reflect global invariants of the system because their properties, e.g., the periods of the orbits, are extremely sensitive to very small changes in the initial conditions; (iv) consider two trajectories corresponding to infinitesimally different initial conditions. In the quasiperiodic motion domain, $E < E_c$, the distance between these trajectories grows linearly with time, whereas in the chaotic motion domain, $E > E_c$, it grows exponentially with time[5]; (v) the Kolmogorov entropy[6-8] of the system, which can be thought of as a measure of the chaos generated by the motion (see Sec. II), is zero in the domain of quasiperiodic motion and positive in the domain of chaotic motion. Moreover, the value of the Kolmogorov entropy is related to the average over the phase space of the characteristic e-folding time for exponential growth of the distance between initially close trajectories.[9]

Consider now the quantum mechanical description of a system which undergoes the classical mechanical quasiperiodic-to-chaotic-motion transition. Is there a change in the character of the stationary states of this system at E_c? If the answer to this question is yes, what are the properties of the stationary states for $E > E_c$?

In order to address the questions just posed we must select a criterion which signals the transition to chaotic behavior. Nordholm and Rice[10] suggested that a state of the system is "ergodic" if an excitation initially not uniformly distributed over the energy surface becomes uniformly distributed as $t \to \infty$. They showed, for several examples which undergo the classical mechanical quasiperiodic-to-chaotic motion transition, that if the eigenstates are represented as a superposition of harmonic oscillator basis states, then there is a "KAMlike" change in the amplitudes of the contributing basis functions at about E_c. Stratt, Handy, and Miller[11] repeated these calculations using the analog of natural orbital basis states to examine the distribution of projections of amplitudes of the eigenstates; they reach the same conclusion as do Nordholm and Rice on the existence of a "KAMlike" transition in the quantum mechanical system. Stratt,

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Handy, and Miller also follow up a suggestion made by Pechukas,[12] and suggest that the nodal pattern of a wave function corresponding to $E > E_c$ is much more "irregular" than the pattern when $E < E_c$. Pomphrey,[13] and later Marcus and co-workers,[14] suggest that for $E > E_c$ the eigenvalues of the system become very sensitive to variation in the coupling that prevents separability of the equation of motion, but that for $E < E_c$ there is very little sensitivity to such variations. The behavior of the nodal pattern of the wavefunction as a function of energy, and of the eigenvalue sensitivity to variation in coupling as a function of energy, both confirm the findings of Nordholm and Rice.

Yet all of the criteria thus far introduced to categorize the behavior of quantum mechanical systems are subjective. For example, although the projections of the wavefunction on to harmonic oscillator or natural oscillator basis functions show a "KAMlike" transition, the wavefunction itself and the corresponding Wigner function do not display any sign of "randomness,"[15] and it is possible to invent separable systems for which the nodal pattern is as "regular" or "irregular" as desired. Furthermore, the evidence from semicalssical quantum theory suggests that only a subset of quasiperiodic trajectories embedded in the domain of chaotic trajectories correlate with eigenstates of the system.[16] Despite the fact that the measure of these particular embedded quasiperiodic trajectories is so very small compared to the measure of all trajectories, they appear to exhaust the eigenvalue spectrum. What then is the meaning of the "KAMlike" behavior of the projections of a full system eigenvector on to some given set of basis vectors?

In order to be able to compare classical mechanical and quantum mechanical chaotic motion, we must introduce some common measure of the chaos. At the qualitative level, the most striking feature of motion in the classically chaotic domain is the exponential divergence of the separation of two trajectories started with infinitesimally different initial conditions. However, because there is no quantum mechanical analog to the classical mechanical trajectory, we cannot use this criterion outside the domain of classical mechanics. On the other hand, we have already noted that the Kolmogorov entropy of a classical mechanical system is related to the average rate of divergence of initially adjacent pairs of trajectories,[9] so if the Kolmogorov entropy can be generalized to the quantum mechanical domain we would have a means of comparing the behavior of a given system when described alternatively by classical and quantum mechanics.

In this paper we develop a generalization of the Kolmogorov entropy suitable for quantum mechanical systems, and examine its behavior in the cases that the eigenvalue spectrum is discrete or continuous. We also examine the quantum dynamics of two models[17,18] previously proposed as examples of systems which undergo a transition to quantum mechanical chaotic motion. We shall show that when the eigenvalue spectrum is discrete both the classical and quantum mechanical Kolmogorov entropy are zero and the corresponding system dynamics is quasiperiodic. In addition, we shall show that the models previously used to demonstrate quantum mechanical chaos have been incompletely analyzed; when exact solutions for the dynamics of these models are obtained the behavior agrees completely with the predictions based on the Kolmogorov entropy. Some implications of these results for the study of intramolecular energy transfer are discussed in the last section of this paper.

II. KOLMOGOROV ENTROPY OF A CLASSICAL MECHANICAL SYSTEM

In this section we consider some of the properties of the Kolmogorov entropy of a classical mechanical system. Our intent is to provide only such information as aids understanding of the extension to quantum mechanical systems made in Sec. III.[19]

The classical mechanical description of a system we use is based on a phase space Γ and a time evolution operator $\hat{U}_t$ defined on that phase space. Given the Hamiltonian equations of motion, Liouville's theorem guarantees that a mapping of the phase space into itself

$$\Gamma_t = \hat{U}_t \Gamma_0 \tag{1}$$

is measure preserving. However, the "shape" of a volume element in phase space can be, and usually is, grossly distorted by successive mappings. Thus, although the motion of each representative point is determined uniquely by the initial conditions and the equations of motion, the relative motion of two points initially close together can appear to be erratic. In a sense, evolution which generates chaotic components of the relative motion can be thought of as a source of random noise. The Kolmogorov entropy is a function defined for the purpose of classifying the extent to which the relative motion is chaotic; it is based on an evaluation of the average amount of uncertainty in the relative location of phase points generated by motion of the system.

To implement the notion that uncertainty is associated with some aspects of the relative motion of points in phase space, we define a partition $\mathcal{P}^{(0)}$ of Γ. This partition consists of a collection of nonempty, nonintersecting sets $\Omega_i^{(0)}$ that completely cover Γ. The volume of phase space associated with $\Omega_i(0)$ is

$$W(\Omega_i^{(0)}) = \int_{\Omega_i^{(0)}} f\, d\Gamma \;, \tag{2}$$

where f is the density of phase points in Γ. The evolution operator $\hat{U}_t$ maps the partition $\mathcal{P}^{(0)}$ into a new partition $\mathcal{P}^{(1)}$ such that

$$\Omega_i^{(1)} = \hat{U}_t\, \Omega_i^{(0)} \;. \tag{3}$$

We associate an information entropy with the partition $\mathcal{P}^{(0)}$ by use of the definition

$$h(\mathcal{P}^{(0)}) \equiv -\sum_i W(\Omega_i^{(0)}) \ln W(\Omega_i^{(0)}) \;. \tag{4}$$

Since $\hat{U}_t W(\Omega_i^{(0)}) = W(\Omega_i^{(0)})$ by Liouville's theorem, we have $h(\mathcal{P}^{(0)}) = h(\hat{U}_t \mathcal{P}^{(0)})$, i.e., the information entropy is conserved under the motion of the system.

Consider, now, two partitions of the phase space Γ, namely, $\mathcal{P}^{(1)}$ and $\mathcal{P}^{(2)}$. From these two partitions we generate the product partition $\mathcal{P}^{(2)} \vee \mathcal{P}^{(1)}$ which consists of all intersections $\Omega_i^{(2)} \cap \Omega_j^{(1)}$. The joint information entropy of the product partition is

$$h(\mathcal{P}^{(2)} \vee \mathcal{P}^{(1)}) = -\sum_{i,j} \pi_{ij} \ln \pi_{ij} , \tag{5}$$

where

$$\pi_{ij} \equiv W(\Omega_i^{(2)} \cap \Omega_j^{(1)}) . \tag{6}$$

We now define the conditional information entropy

$$h(\mathcal{P}^{(2)} | \mathcal{P}^{(1)}) \equiv -\sum_{i,j} \pi_{ij} \ln \left(\frac{\pi_{ij}}{W(\Omega_j^{(1)})} \right) . \tag{7}$$

which refers to the overlap between the partitions $\mathcal{P}^{(2)}$ and $\mathcal{P}^{(1)}$. Note that when $\mathcal{P}^{(2)} = \mathcal{P}^{(1)}$, $h(\mathcal{P}^{(2)} | \mathcal{P}^{(1)}) = 0$. Therefore, if $\mathcal{P}^{(2)} = \hat{U}_t \mathcal{P}^{(1)}$, we can take $h(\mathcal{P}^{(2)} | \mathcal{P}^{(1)})$ to be a measure of the distortion in the shape of the volume element generated by evolution under the equation of motion. Proceeding in an analogous fashion, we define the joint partition $\mathcal{P}_n$ as the *product* of all the partitions produced by evolution for n time steps under the equation of motion

$$\mathcal{P}_n \equiv \mathcal{P}^{(0)} \vee \hat{U}_t \mathcal{P}^{(0)} \vee \hat{U}_t^2 \mathcal{P}^{(0)} \vee \cdots \vee \hat{U}_t^n \mathcal{P}^{(0)} , \tag{8}$$

and we define the average entropy per time step for a given partition $\mathcal{P}^{(0)}$ and evolution operator $\hat{U}_t$ by the limiting process

$$h(\mathcal{P}^{(0)}, \hat{U}_t) \equiv \lim_{n \to \infty} \frac{1}{n} h(\mathcal{P}_n) . \tag{9}$$

If $\hat{U}_t$ is the identity operator, $\hat{U}_t^n \mathcal{P}^{(0)} = \mathcal{P}^{(0)}$, and since $h(\mathcal{P}^{(0)})$ is finite, taking the limit in (9) gives $h(\mathcal{P}^{(0)}, \hat{U}_t) = 0$. At the other extreme, if all the successive partitions are independent, it can be shown that $h(\mathcal{P}^{(0)}, \hat{U}_t) = h(\mathcal{P}^{(0)})$.

The average entropy per time step can also be represented in the form[20]

$$h(\mathcal{P}^{(0)}, \hat{U}_t) = \lim_{n \to \infty} h(\mathcal{P}^{(n)} | \mathcal{P}^{(0)} \vee \mathcal{P}^{(1)} \vee \cdots \vee \mathcal{P}^{(n-1)}) , \tag{10}$$

which can be utilized as follows: if, under a long succession of mappings, the partition $\mathcal{P}^{(n)}$ cannot be completely inferred from the previous $n-1$ partitions, then $h(\mathcal{P}^{(0)}, \hat{U}_t) > 0$ and the motion of the system is considered chaotic; if the converse is true $h(\mathcal{P}^{(0)}, \hat{U}_t) = 0$ and the motion of the system is quasiperiodic. The Kolmogorov entropy is designed to represent only the chaotic properties of the motion generated by the evolution operator $\hat{U}_t$. Given all possible partitions of the phase space $\boldsymbol{\Gamma}$, the Kolmogorov entropy is defined by

$$h_K \equiv \sup_{\mathcal{P}} h(\mathcal{P}, \hat{U}_t) . \tag{11}$$

That is, by that partition which maximizes the average entropy per time step for given $\hat{U}_t$.

The Kolmogorov entropy of a classical mechanical system can be shown to have the following properties: (i) h_K is invariant to an isomorphism of the evolution operator $\hat{U}_t$, so that if desired an analagous motion on a different space can be used to calculate its value[6-8]; (ii) it is found that[6-8]

$$h_K(\hat{U}_t^n) = n h_K(\hat{U}_t) , \tag{12}$$

from which one can draw two important inferences. First the Kolmogorov entropy per time step is invariant to the time scale and, second, if the motion is periodic for a finite number of time steps n, the Kolmogorov entropy is zero. The first inference follows from division of both sides of Eq. (12) by n, while the second is a consequence of the fact that for a periodic evolution operator $\hat{U}_t^m = 1$ for some m, and every partition is invariant under the identity operator $\hat{1}$; (iii) in a mixing system, for which $h_K > 0$, a small region of phase space of volume W will become uniformly distributed with e-folding time $-\ln W / h_K$. To be more specific, the exponential rate of divergence of pairs of initially adjacent trajectories is measured by the Liapanov characteristic number $\chi(\Gamma)$, where Γ is a point in the phase space $\boldsymbol{\Gamma}$. A remarkable theorem by Piesen[9] relates the Liapanov number to the Kolmogorov entropy

$$h_K(\hat{U}_t) = \sum_i \int \chi_i(\Gamma)\, d\boldsymbol{\Gamma} . \tag{13}$$

The sum in (13) is over all vectors along the tangent mapping of the evolution operator for which $\chi(\Gamma) > 0$; Piesen shows that there can be no more than $N-1$ of these vectors for a system with N degrees of freedom.[9] Equation (13) establishes a link between the mechanical notion of diverging trajectories and the entropic measure of the chaotic properties of the system evolution under the given equation of motion.

III. KOLMOGOROV ENTROPY OF A QUANTUM MECHANICAL SYSTEM

The first step in the extension of the Kolmogorov entropy concept to quantum mechanical systems is the definition of a quantum mechanical analog of the partition $\mathcal{P}$ defined on the phase space $\boldsymbol{\Gamma}$. A few obvious but necessary remarks are a preamble to our argument.

A quantum mechanical description of a system is based on a Hilbert space $\mathcal{H}$, a positive density operator with unit trace $\hat{\rho}$, and a set of operators $\{\hat{A}\}$ on the Hilbert space defined to represent physical observables. The density operator represents the state of the system, and the expectation value of an observable A is just $\mathrm{Tr}(\hat{\rho}\hat{A})$. It is convenient to think of the evolution of the system under the equation of motion as a trace preserving mapping of density operators into density operators. Then the state of the system at time t_2 is obtained from the state at time t_1 by the transformation

$$\hat{\rho}(t_2) = \mathrm{Tr}_1[\hat{U}_{12} \hat{\rho}(t_1)] , \tag{14}$$

where $\hat{U}_{12}$ is the evolution superoperator and Tr_1 is the trace operation with respect to $\hat{\rho}(t_1)$. An operator $\hat{A}$ admits a spectral resolution into a set of orthogonal projection operators

$$\hat{A} = \sum_i \alpha_i \hat{P}_{A_i} . \tag{15}$$

Given the set of projection operators $\{\hat{P}_{A_i}\}$ we can construct a resolution of the identity operator in the form

$$\hat{1} = \sum_i \hat{P}_{A_i} . \tag{16}$$

The set of projection operators $\{\hat{P}_{A_i}\}$ describes all the distinct outcomes that can be realized when the expectation value of $\hat{A}$ is observed.

We now define the set of orthogonal projection operators $\{\hat{P}_{A_i}\}$ which resolve the identity operator to be the quantum mechanical analog of the partition $\mathcal{P}$ on the classical mechanical phase space Γ. Furthermore, we define the entropy associated with an observable A (Ref. 21) in a state k as the amount of uncertainty in $\hat{\rho}$ resolved by the measurement of A, i.e.,

$$h(\hat{\rho}, \hat{A}) \equiv -\sum_k p_k \ln p_k \tag{17}$$

where

$$p_k \equiv \mathrm{Tr}(\hat{\rho}\,\hat{P}_{A_k}) . \tag{18}$$

In addition to an analog of a partition on the phase space, we must also define an average entropy per unit time. To do so, we must construct the joint probability of obtaining from a series of measurements of A the outcome α_1 at t_1, α_2 at $t_2, \ldots,$ α_n at t_n. Imagine an ensemble of identical systems in a state defined by the density operator $\hat{\rho}$. At each of the times $t_1, t_2, \ldots, t_n$ a sample is extracted from the ensemble and the observable A measured; after each extraction of a sample the remainder of the ensemble is allowed to evolve undisturbed. The Hilbert space on which the joint probability of obtaining α_1 at t_1, α_2 at $t_2, \ldots$ is defined as the tensor product space

$$\mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \otimes \mathcal{H}^{(3)} \otimes \cdots \otimes \mathcal{H}^{(n)} , \tag{19}$$

on which we can define the density operator

$$\hat{\rho}_n \equiv \hat{\rho} \otimes \hat{U}\hat{\rho} \otimes \cdots \otimes \hat{U}^n \hat{\rho} . \tag{20}$$

The combined density operator $\hat{\rho}_n$ describes the correlated state of the system for all the times $t_1, t_2, \ldots, t_n$. Given Eq. (20), the required joint probability is defined by

$$\begin{aligned}\mathcal{P}(A^{(1)} &= \alpha_1, \ldots, A^{(n)} = \alpha_n) \\ &= \mathrm{Tr}_{1,2,\ldots,n}(\hat{P}_{A_1^{(1)}} \otimes \hat{P}_{A_2^{(2)}} \otimes \cdots \otimes \hat{P}_{A_n^{(n)}}\,\hat{\rho}_n) ,\end{aligned} \tag{21}$$

where the $A^{(l)}$ refer to the observable A at time t_l. Note that the projection operators in the argument of the trace of Eq. (21) are at different times, hence they commute, and their ordering is not important.

We can now define the average information entropy associated with measuring the observable A as

$$h(\hat{U}, \hat{A}, \hat{\rho}) \equiv \lim_{n\to\infty} \frac{1}{n}\, h(\hat{A}_n, \hat{\rho}_n) , \tag{22}$$

where

$$\hat{A}_n \equiv \hat{A}^{(1)} \otimes \hat{A}^{(2)} \otimes \cdots \otimes \hat{A}^{(n)} . \tag{23}$$

From the set of all possible operators corresponding to observables we choose that one which maximizes $h(\hat{A}, \hat{\rho})$. Thus, our quantum mechanical generalization of the Kolmogorov entropy is defined by

$$h_K(\hat{U}) \equiv \sup_{\hat{A}}\, h(\hat{U}, \hat{A}, \hat{\rho}) . \tag{24}$$

This definition of h_K is quite general; note that it does not depend on how chaos is generated[22] and, since it is based on a classical probability space, most of the theorems which describe the behavior of the classical mechanical Kolmogorov entropy apply equally well to the quantum mechanical extension (24). In particular, Eq. (12) remains valid for both the quantum mechanical and classical mechanical Kolmogorov entropy.

We now note that our definition (24) implies there is an important difference between the behavior of classical mechanical and quantum mechanical systems with respect to the onset of chaotic motion. For, if the spectrum of a unitary evolution operator is discrete, the Kolmogorov entropy of the corresponding motion is zero. Because of its importance, we will sketch the proof of this statement.

If the evolution operator has a discrete spectrum, it can be expanded in terms of a set of orthogonal projectors in operator space. We write, for one unit time interval T,

$$\hat{U}_T = \sum_j \hat{g}_j e^{i\Delta_j T} , \tag{25}$$

where $\hat{g}_j$ is the amplitude and $\Delta_j T$ is the phase of projector j. Clearly, the evolution operator corresponding to a time interval nT is

$$\hat{U}_T^n = \sum_j \hat{g}_j e^{i\Delta_j nT} \tag{26}$$

and it is possible to find a number n such that $\hat{U}^n$ is as close to the identity operator as desired. Then, using Eq. (12), the Kolmogorov entropy is zero.

The inference that the Kolmogorov entropy is zero when the evolution operator has a discrete spectrum is true in both quantum mechanics and classical mechanics. Nevertheless, there are important differences between classical and quantum mechanical motion on the same potential surface. Thus, if we consider motion of a bounded system, the spectrum of the quantum mechanical evolution operator is always discrete, whereas that of the classical mechanical evolution operator is discrete in the quasiperiodic domain and continuous in the chaotic domain. We note that in this case of bounded motion, there will usually be a regime in which classical mechanical trajectories diverge and the corresponding Kolmogorov entropy is positive, while at the same energy the quantum mechanical Kolmogorov entropy is zero. Therefore, for bounded motion on the same potential surface, chaotic classical mechanical motion does not have a quantum mechanical analogue. Of course, in the limit that $\hbar \to 0$ the quantum mechanical evolution operator's spectrum can become continuous even for bounded motion, and in that case the limiting classical mechanical motion is chaotic. If when $\hbar \to 0$ the spectrum of the evolution operator remains discrete, the limiting classical mechanical motion is quasiperiodic.

IV. COMPARISON OF THE CLASSICAL AND QUANTUM MECHANICAL KOLMOGOROV ENTROPIES

In this section we discuss some aspects of the relationship between the classical mechanical and quantum mechanical concepts involved in defining the Kolmogorov entropy. Given the nature of these concepts, we show how the von Neumann axiomatic formulation of quantum mechanics[23] leads to our formulation of the Kolmogorov entropy.

Consider, first, the prescription used to define the classical mechanical Kolmogorov entropy, namely, the successive partitioning of the phase space $\mathbf{\Gamma}$. Recall that the microstate of a classical mechanical system can be represented by a point Γ in the space $\mathbf{\Gamma}$, and the evolution of the microstate of the system by the trajectory $\Gamma(t)$ that satisfies the equation of motion for the given initial conditions. Any particular partition $\mathcal{P}^{(0)}$, which consists of a collection of nonempty nonintersecting sets that completely cover $\mathbf{\Gamma}$, also defines a set of macrostates of the system, each macrostate consisting of all the microstates whose representative points lie within one of the sets of points of $\mathbf{\Gamma}$ generated by that particular partition. Thus, a partition $\mathcal{P}^{(0)}$ of the phase space $\mathbf{\Gamma}$ can be thought of as a specification of the set of all possible outcomes of an experiment which, at time t_0, determines the macrostate of the system. Put another way, the possible outcomes of an observation of the macrostate of the system are mapped, by the definition of the partition $\mathcal{P}^{(0)}$, into the corresponding sets of points which represent those macrostates.

The partitioning of the phase space $\mathbf{\Gamma}$ leads to the consideration of a classical (Kolmogorov) probability space. This probability space consists of a triple ($\mathbf{\Gamma}$, Ω, μ), where the elements $\mathbf{\Gamma}$ correspond to the possible outcomes of a random experiment, the sets in Ω correspond to random events and the measure $\mu(A)$ for $A \in \Omega$ gives the probability that the random event occurs. Given the probability space ($\mathbf{\Gamma}$, Ω, μ), a random variable corresponds to a measurable quantity for the random experiment. If B is some subset of the possible outcomes, and f is a random variable, $f^{-1}(B)$ is the event that f has a value in B and $[\mu_f \equiv \mu f^{-1}(B)]$ is the probability of that event. Clearly, μ_f is the distribution of f. The expectation value of f is defined in the usual way as $\int f d\mu$. In classical probability theory, successive observations do not interfere with one another and the corresponding random variables commute. Thus, in the product partition defined in Eq. (8), the ordering of the component partitions is irrelevant.

We now consider the prescription proposed for the definition of the quantum mechanical Kolmogorov entropy. Our construction is based on the following axiom[23-26]:

The probability that an observable A has a value in a (Borel) set B when the system is in the state described by ψ is $\langle \hat{P}_A(B)\psi, \psi\rangle$, where $\sum_B \hat{P}_A(B) = \hat{1}$ is the resolution of the identity operator for $\hat{A}$ [see Eqs. (15) and (16)]. Thus $\langle \hat{P}_A(B)\psi, \psi\rangle$ is the distribution of the observable A in the state ψ, and comparison of the classical and quantum mechanical definitions shows that observables correspond to random variables, and that projection operators $\hat{P}_A(B)$ correspond to events. It can be shown that any finite number of observables can be treated as random variables if and only if they commute.[27] We may in general interpret the set $\{\hat{P}\}$ of orthogonal projections on a Hilbert space $\mathcal{H}$ as a set of quantum mechanical events. Note that there is a one-to-one correspondence between orthogonal projections and closed subspaces of $\mathcal{H}$ so that said set of closed subspaces can also be considered quantum mechanical events. Although the preceding has been stated for the case that the system is in a pure state represented by ψ, the argument is easily extended to the case that the state of the system is represented by the density operator $\hat{\rho}$. To do so we need only note that the mapping $\hat{P} \to \langle \hat{P}\psi, \psi\rangle$, $\hat{P} \in \{\hat{P}\}$, which replaces the classical probability measure μ when the system is in a pure state, is itself replaced by $\hat{P} \to \mathrm{Tr}(\hat{\rho}\hat{P})$ when the system is in the mixed state represented by the density operator $\hat{\rho}$.

In summary, if $\mathcal{H}$ is a Hilbert space, $\{\hat{P}\}$ is the set of orthogonal projections on $\mathcal{H}$, and $\hat{\rho}$ is a density operator with unit trace, then the triple ($\mathcal{H}$, $\{\hat{P}\}$, $\hat{\rho}$) is the quantum probability counterpart to the classical probability space ($\mathbf{\Gamma}$, Ω, μ). In terms of this counterpart we have the following strong theorem[26]:

If ($\mathbf{\Gamma}$, Ω) is a measurable space, there exists a Hilbert space $\mathcal{H}$ and a σ isomorphism T_σ from Ω to the set $\{\hat{P}\}$ of orthogonal projections on $\mathcal{H}$. For any probability measure μ on ($\mathbf{\Gamma}$, Ω) there exists a density operator $\hat{\rho}$ such that $\mu(\Omega) = \mathrm{Tr}[T_\sigma(\Omega)\rho]$ for every $\Omega \in \mathbf{\Gamma}$. For any class of random variables $\{f_\alpha\}$ on ($\mathbf{\Gamma}$, Ω) there exists a class of observables $\{A_\alpha\}$ such that $\hat{P}_{A_\alpha}(E) = T_\sigma[f_\alpha^{-1}(E)]$ for every E contained in the Borel subsets of $\mathbf{\Gamma}$.

Examination of our procedure for the construction of the quantum mechanical Kolmogorov entropy shows that it is in one-to-one correspondence with the classical mechanical Kolmogorov entropy. In particular, the definition displayed in Eq. (21) guarantees the commutation of the projection operators, hence permits treatment of the observables as random variables.

The definition of the quantum mechanical Kolmogorov entropy which we propose differs somewhat from those introduced by Connes and Stormer, Emch, and Lindblad.[22] Connes and Stormer, and also Emch, construct a noncommutative counterpart of the classical partition; in our construction, by virtue of the sampling method by which measurements are made, measurements at different times do not interfere with each other. It is only when this condition is met that a classical probability space can be defined. Lindblad, and also Emch, uses an external bath to generate a stochastic force on the system, which force plays a role in the definition of the entropy. The lattice structure of his definition resembles ours, but there is no reference made to the observables of the system. In view of these remarks, we conclude that our definition of the quantum mechanical Kolmogorov entropy is in closer correspondence with the classical Kolmogorov entropy than those previously proposed, and is more general.

V. TWO MODELS COMPARING CLASSICAL AND QUANTUM MECHANICAL CHAOS

The conclusion that the Kolmogorov entropy of a quantum mechanical system with discrete energy level spectrum is zero conflicts with the suggestion of a "KAMlike" transition in the projection of the system wave function onto a set of basis states, and also with the results of the analyses of two model systems designed for the purpose of comparing the nature and onset of classical mechanical and quantum mechanical chaotic motion. In this section we reexamine the behavior of the model systems proposed by Berry, Balazs, Tabor, and Voros[17] (BBTV) and by Casati, Chirikov, Izraelev, and Ford[18] (CCIF); we reserve for the discussion of Sec. V our reinterpretation of the results of the calculations of Nordholm and Rice,[10] Stratt, Handy, and Miller,[11] and Marcus.[14]

A. BBTV model

Berry, Balazs, Tabor, and Voros[17] have proposed a model Hamiltonian, which defines a class of one dimensional systems, for which it is possible to study both the area preserving mappings on the classical mechanical phase space and the corresponding quantum mechanical evolution generated by unitary transformations of the system wavefunction (called a quantum mapping by BBTV). This Hamiltonian is periodic, with period T, and its time average describes a particle of mass μ moving in a potential $V(q)$. They write

$$\begin{aligned} &\hat{H}(\hat{q}, \hat{p}, t)=\hat{p}^2/2\mu\gamma \quad (0<t<\gamma T) , \\ &\hat{H}(\hat{q}, \hat{p}, t)=\hat{V}(\hat{q})/(1-\gamma) \quad (\gamma T<t<T) , \end{aligned} \tag{27}$$

and

$$\overline{H}(\hat{q}, \hat{p})=\hat{p}^2/2\mu+\hat{V}(\hat{q}) . \tag{28}$$

Note that when γ is close to unity the Hamiltonian (27) is that of a free particle which is periodically perturbed with a potential $\hat{V}(\hat{q})\,\delta_p(t/T)$, where $\delta_p(t/T)$ is a periodic delta function which "turns on" for an infinitesimal interval energy T sec. Given this particular perturbation, the energy is alternately purely kinetic or purely potential. The quantum mapping operator, which describes the action of $\hat{H}$ for the interval $t=0$ to $t=T$, is found to be

$$\hat{G}(\psi)=\hat{U}_T\psi\,\hat{U}_T^\dagger , \tag{29}$$

$$\hat{U}_T=\exp\left(-\frac{iT}{\hbar}\,\hat{V}(\hat{q})\right)\exp\left(-\frac{iT}{2\mu\hbar}\,\hat{p}^2\right) . \tag{30}$$

The classical mechanical motion of the system is described by the same Hamiltonian with the operators $\hat{q}$ and $\hat{p}$ replaced by the corresponding conjugate variables. The mapping of the phase space generated by this Hamiltonian for the time interval $t=nT$ to $t=(n+1)\;T$ is

$$q^{(n+1)}=q^{(n)}+(p^{(n)}/\mu)\,T , \tag{31}$$

$$p^{(n+1)}=p^{(n)}-TV'(q^{(n+1)}) \tag{32}$$

where $V'(q)$ is the derivative of V with respect to q.

We consider the case that $\hat{V}(\hat{q})$ is quadratic in $\hat{q}$,

$$\hat{V}(\hat{q})=\tfrac{1}{2}\,\mu\omega^2\hat{q}^{\,2} , \tag{33}$$

for which the classical map $X^{(n+1)}=MX^{(n)}$ is linear

$$M=\begin{pmatrix} 1 & T/\mu \\ -\mu\omega^2 T & 1-\omega^2 T \end{pmatrix} . \tag{34}$$

A calculation of the effect of the operation of $\hat{G}$ on $\hat{p}$ and $\hat{q}$ leads to the same result as the classical mechanical mapping (34). We now determine the spectrum of the evolution operator $\hat{G}$. The first step is to calculate the eigenvalues and eigenoperators of M; we find

$$\hat{G}\hat{I}_{1,2}=\lambda_{1,2}\hat{I}_{1,2} , \tag{35}$$

where

$$\hat{I}_{1,2}=\hat{q}+\beta_{1,2}\hat{p} \tag{36}$$

and

$$\lambda_{1,2}=-1-\tfrac{1}{2}\,\omega^2T\pm i\omega(1-\tfrac{1}{4}\,\omega^2T^2)^{1/2} , \tag{37}$$

$$\beta_{1,2}=\pm(i/\mu\omega)(1-\tfrac{1}{4}\omega^2T^2)^{1/2} . \tag{38}$$

We now define the operator $\hat{N}=\hat{I}_1\hat{I}_2$, which is an invariant of motion, as can be seen from the relation

$$\hat{G}\hat{N}=\hat{U}_T\hat{I}_1\hat{I}_2\hat{U}_T^\dagger=\hat{U}_T\hat{I}_1\hat{U}_T^\dagger\hat{U}_T\hat{I}_2\hat{U}_T^\dagger=\lambda_1\lambda_2\hat{I}_1\hat{I}_2 . \tag{39}$$

Because it is an invariant of the motion, $\hat{N}$ plays a role similar to that played by the Hamiltonian in the sense that $\hat{N}$ commutes with $\hat{U}_T$ and therefore $\hat{N}$ and $\hat{U}_T$ have a common set of eigenfunctions. Clearly, when the spectrum of $\hat{N}$ is continuous, the spectrum of $\hat{G}$ will also be continuous. Writing out $\hat{N}$ explicitly we find

$$\hat{N}=\hat{q}^2+[(1-\tfrac{1}{4}\omega^2T^2)/\mu^2\omega^2]\hat{p}^2 . \tag{40}$$

Note that $\hat{N}$ resembles the Hamiltonian of a harmonic oscillator with the modified frequency

$$\omega'=\tfrac{1}{2}\mu\omega^2/(1-\tfrac{1}{4}\omega^2T^2) . \tag{41}$$

Now, the spectrum of an oscillator is discrete if $\omega'>0$, in which case we recover the BBTV condition of stability. But if $\omega'<0$, the harmonic potential is inverted (has negative curvature), in which case the spectrum is continuous and the mapping is unstable. Thus, there appears to be complete correspondence between the classical mechanical and quantum mechanical mappings and onset of chaotic motion. The motion becomes mixing for the same values of T and ω, just where the spectrum of the system becomes continuous. However, this correspondence may be misleading for three reasons:

(i) It is hard to imagine a physical process in which the motion consists alternately of segments with purely kinetic and purely potential energy. This is because there is no zero order Hamiltonian which corresponds to such a motion, and therefore it is difficult to consider energy changes in the system. A more realistic model is one in which a free particle with the zero order Hamiltonian

$$\hat{H}_0=\hat{p}^2/2\mu \tag{42}$$

is perturbed by the periodic time dependent potential

$$\hat{V}(t)=\mu\omega^2\hat{q}^2\delta_p(t/T) . \tag{43}$$

The equation of motion for this system can be solved exactly. One finds that the motion is stable for all values of T when $\omega>0$, and that the spectrum of the system is discrete.

(ii) In order for the motion in the system to be mixing, it is necessary that the evolution operator have a continuous spectrum. In a quantum mechanical description this condition implies that the motion is unbounded, and therefore we can not define a compact probability space.

In classical mechanics the difficulty posed by unbounded motion is overcome by defining a modified mapping with periodic boundary conditions,[4] e.g., a mapping of the unit square into itself. This procedure produces a compact space which preserves the ergodic characteristics of the full dynamics. Because of the compactness of the space, the Kolmogorov entropy can then be calculated. For the linear map (34) the Kolmogorov entropy is found to be positive.[4] Of course, if we change the boundary conditions of the quantum mechanical system we also change the dynamics; under cyclic boundary conditions the spectrum is always discrete, hence the mixing properties of the motion are lost.

(iii) The BBTV model is closer to a classical mechanical description than is at first apparent from the formalism. For, the definition of the Hamiltonian (27) implies that at the same time t either the potential or the kinetic energy is zero, so the commutator of the potential and kinetic energy operators vanishes. In this sense, the model omits an essential feature of the quantum dynamics of all ordinary systems.

B. CCIF model: Periodically perturbed pendulum

The system discussed by Casati, Chirikov, Izraelev, and Ford[18] has the classical mechanical Hamiltonian

$$H = p_\theta^2/2\mu l^2 - (\mu l^2 \omega_0^2 \cos\theta)\,\delta_p(t/T)\ , \tag{44}$$

where θ is the angular displacement and p_θ is the corresponding angular momentum; μ, l, and ω_0 are the mass, length, and small amplitude frequency of the pendulum, respectively; and $\delta_p(t/T)$ is, as before, a periodic delta function. Let $\theta^{(n)}$ and $p_\theta^{(n)}$ be the values of θ and p_θ just prior to the nth application of the perturbing force. Direct integration of the equations of motion for $\dot\theta$ and $\dot p_\theta$ yields

$$\tilde p^{(n+1)} = \tilde p^{(n)} - K\sin\theta^{(n)}\ , \tag{45}$$

$$\theta^{(n+1)} = \theta^{(n)} + \tilde p^{(n+1)}\ , \tag{46}$$

where $\tilde p^{(n)} \equiv p_\theta^{(n)} T/\mu l^2$ and $K \equiv (\omega_0 T)^2$. In the limit $K \to 0$ the trajectories of this system are periodic, since the system is then an ordinary conservative, gravitational pendulum. When K is small most of the trajectories are quasiperiodic, as implied by the KAM theorem. However, when $K \gg 1$ the trajectories are chaotic and the motion of $\tilde p$ is diffusive.

To solve the equivalent quantum mechanical problem CCIF note that the system can be regarded as a perturbed rigid rotor. It is, therefore, convenient to expand the wave function for the perturbed system in free rotor basis functions

$$\psi(\theta, T) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} A_n(t)\, e^{in\theta}\ . \tag{47}$$

Integration of the quantum mechanical equation of motion for one period T defines a unitary transformation that relates the wave functions at times t and $t+T$. In the momentum representation this transformation is given by

$$A_n(t+T) = \sum_{r=-\infty}^{\infty} A_r(t)\, b_{n-r}(k)\, e^{-ir^2\tau/2}\ , \tag{48}$$

where

$$b_s(k) = b_{-s}(k) \equiv i^s J_s(k)\ , \tag{49}$$

$$k \equiv \mu l^2 \omega_0^2 T/\hbar\ , \tag{50}$$

$$\tau \equiv \hbar T/\mu l^2\ , \tag{51}$$

and $J_s(k)$ is a Bessel function of the first kind. CCIF have numerically integrated the quantum mechanical equation of motion for many periods T. The results of these calculations show an evolution in time which is significantly different from the time evolution of the corresponding classical mechanical system. Details of the behavior are discussed in Ref. 18, and we here single out only two points. First, the classical mechanical motion is parametrized by the single variable $K = k\tau$, whereas the quantum mechanical motion depends separately on k and τ. Second, and more striking, for particular values of τ the quantum mechanical motion is deterministic even though the classical motion is chaotic for the corresponding value of $k\tau$, e.g., when $\tau = 4\pi$ the motion is strictly periodic. These findings have a simple explanation in terms of the differences between the quantum mechanical and classical mechanical descriptions of the system.

The model under consideration has two periodicities that generate constraints on the quantum dynamics not present in the classical dynamics of the system. First, the periodicity of the potential in θ, just as in the case of motion in a regular lattice, leads to a constraint on the relationship between p_θ and θ and restricts changes in p_θ to multiples of the basic wave vector of the system. In our case, when the coordinate is an angle, that basic wave vector corresponds to an angular momentum

$$p_0 = \hbar\ . \tag{52}$$

Second, the periodicity of the potential in time leads to a constraint on energy transfers, all of which must be a multiple of the unit energy

$$E_0 = h/T\ . \tag{53}$$

The existence of the unit momentum and unit energy can also be thought of as the consequence of satisfying the uncertainty relations for a potential with the angular and temporal periodicities of our model.

Let $p_\theta^{(n)}$ and $E^{(n)}$ be the angular momentum and energy prior to the nth application of the perturbing force. Since the angular momentum and energy can change only by integer amounts, we have

$$(1/2ml^2)(m_1 p_0 + p_\theta^{(n)})^2 = m_2 E_0 + E^{(n)}\ , \tag{54}$$

where m_1 and m_2 are integers. Equation (54), which plays the role of a selection rule, greatly restricts the response of the system to the perturbation. Indeed, for each initial state characterized by $p_\theta^{(n)}$ and $E^{(n)}$ there is a particular set of final states, characterized by those integer values of m_1 and m_2 that satisfy Eq. (54). The composition of this set of final states, that is the distribution with respect to m_1 and m_2, is very sensitive to the values of $p_\theta^{(n)}$ and $E^{(n)}$, and also to the value of T. In this sense the quantum mechanical solution retains the sensitivity to initial conditions characteristic of the corresponding classical solution in the chaotic domain. Nevertheless, the eigenvalues of energy and angular momentum are well defined and simply related, so the corresponding motion is not well described if called chaotic. The importance of Eq. (54) is readily illustrated by interpretation of the observations that when $\tau = 4\pi$ the motion of the system is periodic and the average energy grows proportional to t^2. For, using Eqs. (51), (52), and (53), we find that when $\tau = 4\pi$, $E_0 = p_0^2/2\mu l^2$, i.e., unit energy and angular momentum are transferred under the perturbation.

The result obtained above recalls the observation that semiclassical quantization appears to satisfactorily reproduce the eigenvalues of a system even when the energy corresponds to a classical trajectory which is deep in the chaotic region.[16] That is, the condition (54) is analogous to the requirement that semiclassical quantization pick out a subset of the quasiperiodic orbits embedded in the chaotic domain, and that the vast majority of the orbits (which are chaotic) are irrevelant to the quantum dynamics.

VI. DISCUSSION

We have shown, by extension of the concept of Kolmogorov entropy, that there is a profound difference between classical mechanical and quantum mechanical systems with respect to the onset of chaotic motion. Yet, as pointed out in Sec. I, numerical investigations of model systems, taken together with the qualitative definitions of chaos previously adopted,[10,11] imply that the onset of chaotic motion is similar in the classical mechanical and quantum mechanical descriptions of a given model system. In this section we attempt to resolve this apparent inconsistency of interpretation.

We begin by returning to the observation, based on the Helleman–Bountis[28] analysis of the Henon–Heiles system, that there is a dense set of periodic trajectories embedded in the chaotic motion domain, and to the inference, based on numerical calculations, that semiclassical quantization of a subset of the periodic and quasiperiodic trajectories exhausts the true eigenvalue spectrum of the system

The inference that only the quasiperiodic trajectories correlate with the eigenstates of the system has been proposed many times. An excellent suggestion (not a proof) as to why this is so has been advanced by Freed[29]; he showed, from a careful examination of the semiclassical approximation to the Green's function of the system, that interference effects destroy the contributions to the action of all but the quasiperiodic trajectories.

Consider, now, a system with two degrees of freedom. Helleman and Bountis characterize the embedded periodic trajectories by the ratio of frequencies σ, which must be a rational fraction, and the Poincaré recurrence time of the system T_r. For a given value of σ the initial conditions that generate embedded periodic trajectories are a smooth function of T_r, but T_r changes discontinuously as a function of σ. Therefore, a small change in initial conditions, which generates a small change in σ, leads to a dramatic change of periodic trajectory topology. It is to be expected that the accommodation of such dramatic changes in topology requires that an embedded trajectory of the type under discussion will span the full phase space in one or a few directions. In contrast, prior to the onset of chaotic motion the closed trajectories sample only a very limited region of the phase space. If a quantum mechanical description of such a system is based on expansion of the system wave function in localized basis functions then, inevitably, more basis functions are needed to represent the wave function in the classical chaotic domain (just to span the necessary region of the phase space) than in the classical quasiperiodic domain. This particular representation of the wave function thus leads to a "KAMlike" transition in the amplitudes of the basis functions, but does not contradict the fundamental result that so long as the spectrum is discrete the motion of the quantum mechanical system is not chaotic.

The preceding remark is a simple version of a more formal analysis which we now sketch. Note that our definition of the quantum mechanical Kolmogorov entropy is based on the use of a sampling measurement procedure. Given this measurement procedure it is possible to assert that the unsampled bulk of the ensemble evolves undisturbed, i.e., for the purpose of our analysis we can consider that the motion of the system is not perturbed by the measurement process. We chose the sampling measurement procedure for just this reason, since in this case the quantum mechanical and classical mechanical concepts of observation are similar. A different measurement procedure leads to a significantly different picture of the evolution of the quantum mechanical system.

Suppose that the expectation value of the operator $\hat{A}$ is measured at the times $t_1, t_2, \ldots, t_n$ on the entire ensemble of systems. Given this procedure, the evolution of the system is altered by the measurement process. Indeed, it is now necessary to consider the system, by virtue of the coupling to the measurement apparatus, to be open, and the assumption that the evolution operator is unitary is no longer valid. Von Neuman[23] proposed that after the expectation value of $\hat{A}$ has been determined the system is described by the reduced density operator

$$\hat{\rho}' = \sum_k p_k(\hat{P}_k \hat{\rho} \hat{P}_k) . \tag{55}$$

In the measurement procedure now under discussion this reduction is accomplished successively at t_1, $t_2, \ldots$, generating density operators $\hat{\rho}'$, $\hat{\rho}''$, ... It has been shown by Kraus[30,31] that successive measurements of the expectation value of $\hat{A}$ in the fashion just described, with free evolution of the ensemble between measurements, generates a semigroup evolution, which is the quantum mechanical analogue of a Markov process. In this case the unitary operator of Eq. (14) is replaced by

$$\hat{G}(\psi) = \sum_k p_k \hat{U}_T(\hat{P}_k \psi \hat{P}_k) \hat{U}_T^\dagger . \tag{56}$$

Our formulation of the quantum mechanical Kolmogorov entropy can equally well be based on the destructive measurement procedure just described; the only change required is the replacement of the unitary evolution operator of Eq. (14) by the semigroup evolution operator of Eq. (56). However, when the Kolmogorov entropy is defined with respect to the semigroup evolution operator (56), a stochastic element which has no classical mechanical analogue is introduced in the analysis. To illustrate this point, consider a linear array of Stern–Gerlach analyzers, each designed to measure the z component of the spin of a particle; a beam of particles is passed from analyzer to analyzer in sequence. Suppose that between each pair of analyzers there is a constant magnetic field in the x direction. The effect of this field is to rotate the particle's spin direction in the yz plane prior to its admission to the next Stern–Gerlach analyzer. It is readily seen that each analyzer acts on the whole ensemble of systems (the beam that passes through). The magnetic field can be adjusted to rotate the spin to any angle θ in the zy plane, and the correlations between successive measurements of the z component of the particle spin depend on the angle θ. In the experiment described the Kolmogorov entropy associated with the evolution of the system can vary from zero when $\theta=0$ to ln2 when $\theta=\frac{1}{2}\pi$, i.e.,

$$h_K = s\left[\sin^2(\tfrac{1}{2}\theta)\right] , \tag{57}$$

where

$$s(x) \equiv -x\ln x - (1-x)\ln(1-x) . \tag{58}$$

It is also important to note that, given the destructive measurement procedure involving the whole ensemble of systems, alteration of the interval between measurements also alters the ensemble's evolution in time. In particular, in the limit that the measurement of the expectation value of $\hat{A}$ is made continuously, the ensemble of systems and measuring apparatus pass into a stationary state, i.e., evolution in time ceases.[32,33]

We now ask if, for a given potential energy surface, the existence of classical mechanical chaotic motion has any significance for the interpretation of the stochastic element introduced by the destructive measurement process of quantum mechanics. To answer this question we imagine constructing a nondestructive measurement of some property of the system out of local observables in phase space; if this is possible the local measurement operator commutes with the effective evolution operator. Now, if the motion of the system is separable, a local measurement of the expectation value of an operator associated with one degree of freedom does not interfere with the evolution of other degrees of freedom. On the other hand, if the motion of the system is not separable, any measurement of the expectation value of an operator associated with only one degree of freedom does interfere with the evolution of the other degrees of freedom. We can use this observation as follows: the calculations of Nordholm and Rice[10] and of Stratt, Handy, and Miller[11] demonstrate that in the region where the classical mechanical motion is chaotic the eigenstates have global character, where by global character we mean that the wave function spans a large region of the phase space, so that correlations between motions in different portions of the phase space cannot be ignored. We conclude that in the domain where the classical motion is chaotic it is not possible to construct a nondestructive local measurement of a property of the corresponding quantum mechanical motion. Since the projection of the system wave function onto basis states can be thought of as a measurement of the amplitudes of localized functions, the existence of a correlation between the onset of classical mechanical chaotic motion and "KAMlike" behavior of the amplitudes of the basis functions is to be expected. Nevertheless, it remains the case that so long as the spectrum of the system is discrete the Kolmogorov entropy is zero and the quantum mechanical motion is not chaotic.

Consider a comparison of the decay of wave packets constructed, respectively, from a superposition of states of a separable system which in the classical limit has quasiperiodic trajectories, and from a superposition of states of a nonseparable system which in the classical limit has chaotic trajectories. In each case the spectrum of the system is assumed to be discrete. We now note that the decay of a wave packet depends only on its spectral content. Then if the spectra of the two systems have similar distributions of states for similar values of the energy, we predict that the rates of decay of the two wave packets will be similar despite the gross difference in behavior of the classical limit trajectories. The calculations of Brumer and Shapiro[34] provide convincing evidence of the validity of this statement. Note that the behavior described derives from the nature of the wave packet, specifically its spectral content. Our use of the Kolmogorov entropy permits this behavior to be anticipated by virtue of the categorization of the consequences of the nature of the spectrum of the system with respect to quasiperiodic and chaotic motion.

In this paper we have focussed attention on the Kolmogorov entropy of a system for which the evolution operator has a discrete spectrum. It can be shown that a necessary but not sufficient condition that the Kolmogorov entropy of a system be positive is that the spectrum of the evolution operator be continuous.[7,8] Given the relationship between the properties of the Kolmogorov entropy and the evolution operator, it is interesting to note that all derivations of the so called Master Equation of which we are aware introduce at some stage of the analysis an approximation, or a limiting condition, which has the effect of making the system's spectrum continuous.[35] It is always assumed in these derivations that a continuous spectrum provides both the necessary and sufficient conditions for irreversible behavior. Yet, the mathematical theory of mixing motion imposes further conditions, and it remains possible that there exist examples for which some types of wave packet initial states do not uniformly sample the full phase space even when the system's spectrum is continuous. This caveat is of considerable importance to the study of intramolecular relaxation processes. It is reasonable to expect the dynamics of a coupled system of many nonlinear oscillators, such as a molecule, to have different kinetic behavior in different energy regions. The obvious extremes are complete dynamical reversibility described by a unitary evolution operator built from the discrete bound state spectrum, and irreversible decay of an initial state described by a relaxation operator determined from the Master equation for the diagonal elements of the density matrix. In between these extremes is a domain in which there might be interesting quantum stochastic dynamics, in the sense that the evolution operator defines a semigroup and a continuous positive mapping of the density operator, but otherwise all interference effects are retained.[36] We speculate that in this quantum stochastic domain there can be special wave packet excitations which do not satisfy the criteria for quasiergodic motion. If a means for exciting wave packets with this behavior can be developed, it may be possible to generate photoselective chemistry even when the spectrum of the molecule is continuous by virtue of overlap of the radiative widths of the energy levels.

Noted added in proof: Perhaps the most direct statement of the thrust of our arguments is the following: Quantum mechanical systems exhibit interference phenomena not found in classical mechanical systems. The difference in behavior of the quantum mechanical and classical mechanical Kolmogorov entropies for a bounded system is one manifestation of those interference effects. If we can learn to use the interference phenomena to alter the time evolution of a wave packet, it may be possible to enhance the photoselectivity of reactions, which is a worthwhile goal to achieve.

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