Time-Dependent Manifestations of Quantum Chaos

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(Received 11 April 1991)

We show that regular and irregular spectral statistics have direct, distinctive, and observable time-dependent manifestations in the behavior of the survival probability $P(t)=|\langle\psi(0)|\psi(t)\rangle|^2$, averaged over Hamiltonian ensembles and initial conditions. Specifically, systems exhibiting energy-level repulsion display characteristically strong decorrelations at short times. The proof relies solely on Liouville spectral properties of ensembles of bound quantum systems.

PACS numbers: 05.45.+b, 03.65.Sq

In the classical mechanics of conservative Hamiltonian systems it is time dependence in general, and the long-time limit in particular, which distinguishes integrable from chaotic dynamics. For example, integrable distributions whose spectral density [1] contains only continuous components relax to long-time limits which depend intimately on the initial conditions whereas the long-time limit in the chaotic case depends only on the energy [2]. Considerations of the long-time limit for dynamical evolution in bound-state quantum mechanics is, however, less useful as a means of distinguishing regular from chaotic dynamics since the long-time dynamics in this case always consists of predetermined contributions from a discrete set of states and hence depends intimately on the initial conditions. Possibly for this reason, relatively little effort has been directed towards distinguishing integrable from chaotic systems on the basis of their quantal time dependence. Rather, work has focused on classifying systems on the basis of statistical properties of the energy spectrum, with regular systems classified [3] as those which display a Poissonian level spacing statistics (i.e., a regular spectrum) and chaotic systems as those which display adjacent level repulsion (an irregular spectrum), etc. Clearly, however, these spectral distinctions are relevant only if they result in clear-cut time-dependent consequences. In this Letter we present rigorous results showing distinctive time-dependent behavior for the dynamics of N-level systems arising from regular versus irregular spectral statistics. Since N may be small we are dealing with true quantum behavior, albeit in the semiclassical energy regime.

Of the few previous studies which have attempted to discern the difference in quantum dynamics of systems with regular versus irregular spectra, several have focused on the survival probability function $P(t)=|\langle\psi(0)|\psi(t)\rangle|^2$, the probability that an initial wave packet will return to itself after time t. Initial studies [4] indicated that the behavior of $P(t)$ depends more upon the choice of $\psi(0)$ than upon the nature of the Hamiltonian. Subsequently, Pechukas examined [5] $\langle\langle P(t)\rangle\rangle$, the survival probability function averaged over both Hamiltonian ensembles and initial wave-function conditions. His study showed a difference, for all time, between $\langle\langle P(t)\rangle\rangle$ for a system with a regular spectrum and $\langle\langle P(t)\rangle\rangle$ for a system with a harmonic-oscillator spectrum, Pechukas' choice for a model for an irregular spectrum. We recently [6,7] improved this irregular model by utilizing Gaussian orthogonal ensemble (GOE) higher level spacing statistics and obtained results in excellent agreement with our computational studies. These results show that $\langle\langle P(t)\rangle\rangle$ for the regular and irregular spectrum cases do differ, but that these differences are confined to short times ($t\simeq 2\pi\hbar/\langle\Delta E\rangle$, where $\langle\Delta E\rangle$ is the average energy-level spacing), the long-time limit being the same in both cases.

In this Letter we utilize general properties of the Liouville spectrum of regular and irregular systems to prove distinctive $\langle\langle P(t)\rangle\rangle$ behavior arising from the spectral statistics. Specifically, we show that $\langle\langle P(t)\rangle\rangle\geq\langle\langle P(\infty)\rangle\rangle$ for systems with a regular spectrum, whereas $\langle\langle P(t)\rangle\rangle$ must fall below $\langle\langle P(\infty)\rangle\rangle$ during its time evolution for systems characterized by level repulsion. Further, we show (1) that the latter result holds for all ensemble-averaged autocorrelation functions in systems with irregular spectra and (2) that the difference in $\langle\langle P(t)\rangle\rangle$ behavior is observable in molecular dynamics using modern spectroscopic techniques on isolated molecules. These proofs rely directly upon the connection between the character of the spectrum of the Liouville operator and the system dynamics, as shown below.

To construct $\langle\langle P(t)\rangle\rangle$ consider an N-dimensional subspace and the associated general wave function

$$|\psi(t)\rangle=\sum_{\alpha=1}^{N}a_\alpha e^{-iE_\alpha t/\hbar}|\alpha\rangle \tag{1}$$

in the basis of energy eigenstates $|\alpha\rangle$. Forming $P(t)$ and averaging over initial conditions [5], i.e., over $\sum_\alpha|a_\alpha|^2$ confined to the unit sphere, gives

$$\langle P(t)\rangle_\psi=\frac{2}{N+1}+\frac{1}{N(N+1)}\sum_{\alpha\neq\beta}\cos(\lambda_{\alpha\beta}t)\,, \tag{2}$$

where $\lambda_{\alpha\beta}=(E_\alpha-E_\beta)/\hbar$. Further averaging over the ensemble of Hamiltonians then gives [6]

$$\langle\langle P(t)\rangle\rangle=\langle\langle|\langle\psi(0)|\psi(t)\rangle|^2\rangle\rangle \tag{3}$$

$$=\frac{2}{N+1}+\frac{2}{N(N+1)}\sum_{r=1}^{N-1}(N-r)p_r(t)\,. \tag{4}$$

Here $p_r(t)=\int_0^\infty d\lambda\cos(\lambda t)p_r(\lambda)$, where $p_r(\lambda)$ is the rth nearest-neighbor energy spacing distribution, i.e., $p_1(\lambda)$ is the nearest-neighbor spacing distribution, $p_2(\lambda)$ is the second-nearest-neighbor spacing distribution, etc. Note that $\langle\langle P(t)\rangle\rangle$ is parametrized by N, the dimensionality of the Hilbert space within which ψ resides and that λ is now a continuous variable. Equation (4) may be rewritten as

$$\langle\langle P(t)\rangle\rangle=\frac{2}{N+1}+\frac{N-1}{N+1}\int_0^\infty d\lambda\, P^N(\lambda)\cos(\lambda t)\,, \tag{5}$$

where, by comparison with Eq. (4),

$$P^N(\lambda)=\frac{2}{N(N-1)}\sum_{r=1}^{N-1}(N-r)p_r(\lambda)\,. \tag{6}$$

It is straightforward to show that $P^N(\lambda)$ is the probability of finding the eigenvalue λ of the quantum Liouville operator. Note first that any frequency of the Liouville spectrum for a bound quantum-mechanical system can be written as a sum of nearest-neighbor spacings [e.g.,

$$(E_{n+r}-E_n)/\hbar$$
$$=(E_{n+r}-E_{n+r-1})/\hbar+\cdots+(E_{n+1}-E_n)/\hbar],$$

and thus each frequency in the Liouville spectrum can be classified according to the number of nearest-neighbor spacings it contains. Let A_i be the event that the Liouville eigenvalue λ is an ith-order spacing. The probability density for λ is then given by

$$P^N(\lambda)=P(A_1\cup\cdots\cup A_{N-1})\,. \tag{7}$$

But since λ cannot be both an ith-order spacing and a jth-order spacing, $P(A_i\cap A_j)=0$ for $i\neq j$. It follows that $P^N(\lambda)=\sum_{i=1}^{N-1}P(A_i)$. There are altogether $N(N-1)/2$ positive spacings in a sequence of N levels, $N-i$ of which are ith-order spacings. Hence the probability of an ith-order spacing is

$$P(A_i)=\frac{2(N-i)}{N(N-1)}p_i(\lambda)\,. \tag{8}$$

Doing the sum over i gives Eq. (6). Hence, Eq. (5) is seen to provide a fundamental relationship between the distribution of Liouville eigenvalues and the dynamical quantity $\langle\langle P(t)\rangle\rangle$.

Consider now $\langle\langle P(t)\rangle\rangle$ for the two cases of the regular and irregular spectrum.

Regular spectrum.—Characteristics of the regular spectrum for an integrable system are known rigorously in the semiclassical limit [3]. Specifically, $p_r(\lambda)$ for the regular spectrum is given by [8]

$$p_r(\lambda)=\left[\frac{\lambda\hbar}{\langle\Delta E\rangle}\right]^{r-1}\frac{\hbar\exp\{-\lambda\hbar/\langle\Delta E\rangle\}}{\langle\Delta E\rangle(r-1)!}\,. \tag{9}$$

Given Eqs. (6) and (9) note first that one can show that

$$\frac{d^2P^N(\lambda)}{d\lambda^2}=\left[\frac{\hbar}{\langle\Delta E\rangle}\right]^3\left[\frac{\hbar\lambda}{\langle\Delta E\rangle}\right]^{N-2}\frac{\exp\{-\lambda\hbar/\langle\Delta E\rangle\}}{(N-2)!} \tag{10}$$

$$\geq 0\,, \tag{11}$$

and that $dP^N(\lambda)/d\lambda<0$ for $\lambda>0$.

To prove that $\langle\langle P(t)\rangle\rangle\geq\langle\langle P(\infty)\rangle\rangle$ we first show that the cosine transform of $P^N(\lambda)$,

$$P^N(t)=\int_0^\infty d\lambda\, P^N(\lambda)\cos(\lambda t)\,, \tag{12}$$

is always greater than or equal to zero. Equation (12) can be integrated by parts to give

$$P^N(t)=P^N(\lambda)\frac{\sin(\lambda t)}{t}\bigg|_0^\infty-\int_0^\infty d\lambda\frac{dP^N(\lambda)}{d\lambda}\frac{\sin(\lambda t)}{t} \tag{13}$$

$$=\int_0^\infty d\lambda\left|\frac{dP^N(\lambda)}{d\lambda}\right|\frac{\sin(\lambda t)}{t}\,, \tag{14}$$

where the second equality holds because $\lim_{\lambda\to\infty}P^N(\lambda)=0$, and $dP^N(\lambda)/d\lambda<0$ for all $\lambda>0$. By dividing the interval $[0,\infty)$ into intervals $[n\pi/t,(n+1)\pi/t)$, for $n=0,1,2,\ldots$, over which $\sin(\lambda t)$ is positive (n even) or negative (n odd) we can sequentially rewrite Eq. (14) as

$$P^N(t)=\sum_{n=0}^\infty(-1)^n\int_{n\pi/t}^{(n+1)\pi/t}d\lambda\left|\frac{dP^N(\lambda)}{d\lambda}\frac{\sin(\lambda t)}{t}\right| \tag{15}$$

$$=\sum_{n=0}^\infty(-1)^nA_n(t)\,, \tag{16}$$

where

$$A_n(t)=\left|\int_{n\pi/t}^{(n+1)\pi/t}d\lambda\frac{dP^N(\lambda)}{d\lambda}\frac{\sin(\lambda t)}{t}\right|. \tag{17}$$

Note now that $A_n(t)\geq A_{n+1}(t)$ since the intervals $[n\pi/t,(n+1)\pi/t)$ are all of equal length, the sine function is symmetric about the centers of the intervals, and $|dP^N(\lambda)/d\lambda|$ is strictly decreasing. Thus every partial sum $\sum_{n=0}^M(-1)^nA_n(t)$, and hence $P^N(t)$, is positive. However, given Eqs. (5) and (12),

$$\langle\langle P(t)\rangle\rangle=\frac{2}{N+1}+\frac{N-1}{N+1}P^N(t)\,, \tag{18}$$

so that $P^N(t)\geq 0$ implies that $\langle\langle P(t)\rangle\rangle$ never falls below its long-time limit of $2/(N+1)$.

Irregular spectrum.—The analytic form for $P^N(\lambda)$ for the irregular case is not known formally, although the GOE model has proven successful in comparison with computational studies [6,8]. To insure complete generality we rely solely upon general properties of $p_r(\lambda)$, with the explicit recognition that the primary characteristic of the irregular spectrum is energy-level repulsion. General properties used below include the following: (a) $p_r(\lambda)$

$\rightarrow 0$ as $\lambda \rightarrow 0$ for $r \geq 2$; (b) $p_r(\lambda) = p_r(-\lambda)$ since the Liouville operator L is unitarily equivalent to $-L$; (c) $p_r(\lambda)$ has a unique maximum on the interval $[0,\infty)$; and (d) $p_1(\lambda) \rightarrow 0$ as $\lambda \rightarrow 0$ for irregular systems since they exhibit level repulsion [9]. Note that the Riemann-Lebesgue lemma guarantees that $p_r(t) = \int_0^\infty p_r(\lambda)\cos(\lambda t) \rightarrow 0$ as $t \rightarrow \infty$. We choose the normalization condition $\int_0^\infty d\lambda\, p_r(\lambda) = 1$ for convenience.

Given these properties it is clear that for ensembles exhibiting level repulsion $P^N(\lambda)$ is increasing over some interval $[0,\lambda^*]$ with a maximum away from zero. This is the case because $P^N(\lambda)$ is of the form $\sum_r c_r p_r(\lambda)$ with $c_r = 2(N-r)/N(N-1) > 0$, each of the $p_r(\lambda)$ is increasing on some interval $[0,\lambda^*]$, and $p_r(\lambda) \rightarrow 0$ as $\lambda \rightarrow \infty$. This simple $P^N(\lambda)$ property, coupled with the following lemma, allows us to demonstrate that in an irregular spectrum case $\langle\langle P(t)\rangle\rangle$ necessarily falls below its asymptotic value.

Lemma.— Let $\hat{f}(\lambda)$ be a function on the interval $[0,\infty)$ with cosine transform $f(t)$. If $f(t)$ is integrable and positive for all t then $\hat{f}(\lambda)$ has a global maximum at $\lambda = 0$.

To show this consider that

$$\frac{2}{\pi}\int_0^\infty dt\, f(t)[1-\cos(\lambda t)] > 0 \tag{19}$$

for $\lambda \neq 0$ and $f(t) \geq 0$. But

$$\frac{2}{\pi}\int_0^\infty dt\, f(t)[1-\cos(\lambda t)] = \hat{f}(0) - \hat{f}(\lambda)\,. \tag{20}$$

Hence, $\hat{f}(0) > \hat{f}(\lambda)$ for $\lambda \neq 0$ and so $\hat{f}(\lambda)$ has a global maximum at $\lambda = 0$.

Applying this result to the irregular $P^N(\lambda)$, with properties as noted above, implies that its cosine transform $P^N(t)$ must go negative and, by Eq. (18), that $\langle\langle P(t)\rangle\rangle$ must fall below its asymptotic value of $2/(N+1)$.

These results provide a clear-cut distinction between the time dependence of systems with regular and irregular spectra [10]. Sample results demonstrating this behavior are shown in Fig. 1 for the case of the (regular) circle billiard and (irregular) stadium billiard. In these computations the average over initial conditions is performed in accord with Eq. (2) and the averaging over Hamiltonians is modeled by an average over J different energy intervals ($J = 100$ for the stadium, $J = 800$ for the circle), each containing N levels. The results, which are in excellent agreement with Poisson- and GOE-based models [6], clearly show much deeper falloff for the irregular case than for the regular case, with the falloff below the asymptote quite apparent. In both these cases the overall $\langle\langle P(t)\rangle\rangle$ behavior is devoid of significant additional structure. However, far more complex $\langle\langle P(t)\rangle\rangle$ behavior (e.g., extreme oscillations), still consistent with the above results, has been observed for both the regular and irregular cases, as discussed elsewhere [6].

The $\langle\langle P(t)\rangle\rangle$ result for the irregular spectrum is easily generalized to any ensemble-averaged autocorrelation function. That is, the autocorrelation function of any observable A is

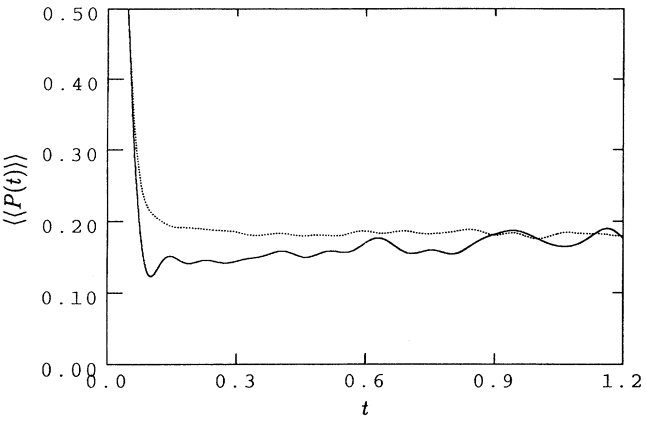

FIG. 1. $\langle\langle P(t)\rangle\rangle$ for the regular circle billiard (dotted curve) and for the irregular stadium billiard (solid curve) for the case of $N = 10$. The slight oscillation of the stadium result is due to the relatively small number (1000) of energy levels used. Normalization is such that $\langle\langle P(0)\rangle\rangle = 1$.

$$C_A(t) = \mathrm{Tr}\{A^\dagger(0)A(t)\} \tag{21}$$

$$= \sum_{n,m} |A_{n,m}|^2 \cos(\lambda_{nm} t)\,, \tag{22}$$

and thus $C_A(t)$ averaged over Hamiltonians [6] is

$$\langle C_A(t)\rangle_H = \sum_n |A_{n,n}|^2 + \sum_r \sum_m |A_{m,m+r}|^2 p_r(t)\,. \tag{23}$$

Since the coefficients $c_r = \sum_m |A_{m,m+r}|^2$ are positive, then $\sum_r \sum_m |A_{m,m+r}|^2 p_r(t)$ must take negative values if the system exhibits level repulsion and hence $\langle C_A(t)\rangle_H$ must fall below its long-time limit. However, in this case such behavior is also possible for autocorrelation functions in regular systems. Thus the survival probability remains of particular interest since its time dependence allows for an unambiguous identification of regular versus irregular spectral statistics and, in addition, it has a transparent connection, via Eq. (5), to the Liouville eigenvalue spectrum.

Finally, we note the possibility of measuring $\langle\langle P(t)\rangle\rangle$ differences for the case of isolated molecule dynamics, a subject of considerable interest in atomic and molecular physics. One route is to examine averages over the stimulated emission spectrum which, assuming the experimental background and linewidths can be properly removed [6], will display $\langle\langle P(t)\rangle\rangle$ directly [11]. Alternatively, $\langle\langle P(t)\rangle\rangle$ can be measured indirectly by measuring the fluorescence intensity $S(t)$ resulting from preparations of many different initial superposition states $\psi_e(t)$ on an excited electronic surface. If these states fluoresce onto M eigenstates $|g_n\rangle$ of the ground electronic surface then the

fluorescence intensity is

$$S(t) \simeq \sum_{n=1}^{M} |\langle g_n | \psi_e(t) \rangle|^2 . \quad (24)$$

Constructing the autocorrelation function $S(t+\tau)S(t)$ for each of the prepared states $\psi_e(0)$ and averaging them to obtain the normalized $C_s(\tau) = \langle S(t+\tau)S(t) \rangle / \langle S(t)S(t) \rangle$ gives the following relationship [6]:

$$C_s(\tau) \simeq \left\{ \frac{M-1}{M} + \frac{\langle\langle P(\tau) \rangle\rangle}{M} \right\} \exp\{-\Gamma\tau/\hbar\} , \quad (25)$$

where $\psi_e(0)$ is comprised of a superposition of N levels and where all eigenstates on the excited electronic surface are assumed to have the same linewidth Γ. Thus $\langle\langle P(t) \rangle\rangle$ associated with N-level preparation can be extracted directly from Eq. (25).

The relationship between these quantum dynamics results and classical integrable versus chaotic time dependence is currently under investigation.

Support from the Centres of Excellence in Molecular and Interfacial Dynamics, and the Ontario Laser and Lightwave Research Center, is gratefully acknowledged. J.W. is a Natural Sciences and Engineering Research Council Postgraduate Fellow.

[1] R. S. Dumont and P. Brumer, J. Chem. Phys. **88**, 1481 (1988).

[2] C. Jaffe and P. Brumer, J. Phys. Chem. **88**, 4829 (1984).

[3] M. V. Berry and M. Tabor, Proc. Roy. Soc. London A **356**, 375 (1977); M. V. Berry, in *Chaotic Behavior of Deterministic Systems,* edited by G. Ioose, R. H. G. Hellman, and R. Stora (North-Holland, Amsterdam, 1983).

[4] P. Brumer and M. Shapiro, Chem. Phys. Lett. **72**, 528 (1980); K. G. Kay, J. Chem. Phys. **72**, 5955 (1980); Y. Weissman and J. Jortner, Chem. Phys. Lett. **78**, 224 (1981); J. S. Hutchinson and R. E. Wyatt, Phys. Rev. A **23**, 1567 (1981).

[5] P. Pechukas, Chem. Phys. Lett. **86**, 553 (1982); J. Phys. Chem. **88**, 4823 (1984).

[6] J. Wilkie and P. Brumer (to be published).

[7] P. Pechukas has also considered related extensions in unpublished work (private communication).

[8] C. E. Porter, Nucl. Phys. **40**, 167 (1963); O. Bohigas, M. J. Giannoni, and C. Schmit, in *Chaotic Behavior in Quantum Systems,* edited by G. Casati (Plenum, New York, 1985).

[9] It suffices, for this proof, that $p_1(\lambda)$ display a local minimum at $\lambda = 0$.

[10] Note that it is possible for a system to have a Liouville spectrum with a global maximum at $\lambda = 0$, and for $\langle\langle P(t) \rangle\rangle$ to fall below its long-time limit. However, such a spectrum cannot be Poisson and hence does not correspond to an integrable system.

[11] C. E. Hamilton, J. L. Kinsey, and R. W. Field, Annu. Rev. Phys. Chem. **37**, 493 (1986); J. M. Gomez Llorente, J. Zakrzewski, H. S. Taylor, and K. C. Kulander, J. Chem. Phys. **90**, 1505 (1989).