Wave packet evolution in isolated pyrazine molecules: Coherence triumphs over chaos

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Recent measurements of the rotational state dependence of the initial fluorescence decay of the vibrationless $^1B_{3u}$ state of pyrazine are analyzed from several points of view. The relationship of these analyses to recent ideas dealing with quantum chaos is discussed.

I. INTRODUCTION

In the accompanying paper[1] to this one we have presented evidence that the radiationless evolution of $^1B_{3u}$ pyrazine is coherent, at least up to some time characteristic of its radiative decay. The argument used to interpret the experiments was based on Green's function techniques and showed that seemingly inconsistent data could be reconciled by simply considering the smoothness of a "self-energy" function. In this paper we will be concerned with the implication of this interpretation as to the existence of chaos in bounded quantum mechanical systems.

To this end the relationship of spectroscopic measurements to the evolution of molecular properties is reviewed using a method of Heller. We then proceed to examine the existence or nonexistence of molecular chaos in pyrazine.

II. WAVE PACKET DYNAMICS

A very perceptive description of the dynamical processes associated with the interaction of light and molecules, particularly fluorescence spectroscopy and Rayleigh–Raman spectroscopy, has been developed by Heller and co-workers.[2–4] This description makes extensive use of the dynamics of wave packet motion on an energy surface.

Heller points out that the usual second order perturbation theory expression for the spontaneous Raman scattering amplitude between rovibrational states $|i\rangle$ and $|f\rangle$ can be rewritten in the form

$$\alpha_{fi}(\omega_I) = \int_0^\infty e^{i(\omega_I+E_i)t-\gamma t}\langle\phi_f|\phi_i(t)\rangle dt + \text{nonresonant term}, \tag{1}$$

where

$$|\phi_i\rangle = \mu_{ab}\cdot\hat{e}_I|i\rangle,$$
$$|\phi_f\rangle = \mu_{ab}\cdot\hat{e}_S|f\rangle, \tag{2}$$

and

$$|\phi_i(t)\rangle = e^{-iH_bt}|\phi_i\rangle. \tag{3}$$

The energy of the incident steady radiation field is ω_I. The derivation of Eq. (1) uses the assumptions that the Born–Oppenheimer (BO) separation is valid and that only two BO states are involved in the scattering. Then μ_{ab} is the transition moment between the lower a and upper b of these states, $\hat{e}_I$ and $\hat{e}_S$ are unit vectors describing the polarization of the exciting and scattered radiation, γ is the radiative lifetime of the upper state, and H_b is the upper state vibrational Hamiltonian. The function ϕ_i is a vibrational wave packet which propagates on the excited state surface; it is not an eigenfunction of H_b. Let

$$R^\infty(\omega_I) = \int_0^\infty \phi_i(t)e^{i(\omega_I+E_i)t-\gamma t}dt. \tag{4}$$

This function, called the Raman wave function by Heller, is a superposition of wave packets with respect to the continuous variable t and with phase factors $\exp[i(\omega_I + E_i)t]$. Assuming that μ_{ab} is independent of vibrational amplitude, it can be shown that the total dispersed fluorescence from the irradiated molecule is

$$I_{\text{TDF}} = \langle R^\infty(\omega_I)|R^\infty(\omega_I)\rangle, \tag{5}$$

aside from the usual frequency factors $(\omega_I\omega_S^3)$ and some constants.

A simple first use of Eq. (5) is to confirm, in different language, the interpretation of the variation of $A_{\text{fast}}/A_{\text{slow}}$ with detuning given in Ref. 1. Note that if $\omega_I + E_i$ is resonant with the particular BO state energy the wave packets displaced with respect to t add constructively and an extended wave function is generated. However, if $\omega_I + E_i$ is detuned from the BO state energy the wave packets displaced with respect to t interfere destructively after an interval Δt equal to the reciprocal of the frequency mismatch. The net results are, of course, that the fluorescence emission is quenched by detuning and that the localized wave packet created by interaction of the mol-

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ecule with a detuned radiation field can only sample a very short section of the time evolution of the system.

Equation (4), which pertains to the case of a steady radiation field, can be extended to describe interaction of a molecule with a pulsed field. Let $a(t)$ be the amplitude as a function of time of the pulsed field. Then we write,

$$R(\omega_I, t) = \lim_{T\to\infty} \int_{-T}^{t} \phi_i(t-u)a(u)e^{i(\omega_I+E_i)(t-u)}e^{-\gamma(t-a)}du. \quad (6)$$

Clearly, $R(\omega_I, t) \to R^{\infty}(\omega_I)$ when $a(u) \to 1$. Consider the function

$$I(\omega_I, t) = \langle R(\omega_I, t)|R(\omega_I, t)\rangle \quad (7)$$

and form

$$W \equiv \lim_{T\to\infty} \frac{1}{T}\int_0^T I(\omega_I, t)dt. \quad (8)$$

In expanded form,

$$I(\omega_I, t) = \int_{-T}^{t} \langle\phi_i|e^{iH_b(t-u')}e^{i(E_i+\omega_I)(t-u')-\gamma(t-u')}a(u')du' \times \int_{-T}^{t} e^{iH_b(t-u)}|\phi_i\rangle e^{i(E_i+\omega_I)(t-u)-\gamma(t-u)}a(u)du. \quad (9)$$

If we insert in Eq. (9) a decomposition of unity in terms of a complete set of states (singlets in our case) and assume that only one such state makes an important contribution to the integral,

$$I(\omega_I, t) = \left| \int_{-T}^{t} \langle\psi_S|\langle S|e^{-iH_b(t-u)}|S\rangle|\psi_S\rangle \times e^{i(E_i+\omega_I)(t-u)}e^{-\gamma(t-u)}a(u)du\right|^2. \quad (10)$$

If the exciting radiation field consists of an on resonance delta function pulse,

$$W = \lim_{T\to\infty} \frac{1}{T}\int_0^T |\langle\psi_S|\langle S|\langle e^{-iH_b t}|S\rangle\psi_S\rangle e^{-\gamma t}|^2 dt = P(S|S). \quad (11)$$

Clearly, $P(S|S)$ is the probability of finding the system in the initially prepared state after an infinite period of time, hence can be used to measure the occurrence of recurrences in the system. Neglecting photon emission (i.e., setting $\gamma = 0$), for an intermediate case molecule such as pyrazine we can write

$$W = \sum_{n=1}^{N} |\langle S|m_n\rangle|^4, \quad (12)$$

where the $\{m_n\}$ are the mixed singlet–triplet levels into which $|S\rangle$ evolves. In the egalitarian coupling model

$$\sum_{n=1}^{N} |\langle S|m_n\rangle|^4 = 1/N. \quad (13)$$

Thus, for this coupling model, the probability of finding the system in the initial state as $t \to \infty$ is only N^{-1}, the same as implied by classical chaos, yet phase coherence of the wave function is maintained for all time.

III. EXISTENCE/NONEXISTENCE OF MOLECULAR CHAOS IN PYRAZINE

We have argued that the time evolution of a wave packet state in $^1B_{3u}$ pyrazine is coherent for a time up to the radiative lifetime. We now invert our argument and ask how this interpretation reflects on the existence or nonexistence of chaos in bounded quantum mechanical systems. We take chaos to mean the loss of phase coherence in the evolution of a state of the molecule, and ask if other signals of chaos are consistent with all of the data for the fluorescence decay of pyrazine.

Pyrazine has 24 vibrational modes. Even though the frequencies of these modes span a considerable range, the existing evidence for mode mixing via Fermi resonance, for Duschinsky rotation, for Coriolis coupling, and the like,[5] suggests that any reasonable classical mechanical model will exhibit chaotic motion at very low total energy.[6] We shall assume this to be the case for a classical mechanical model of pyrazine at the energy characteristic of the mixed single–triplet levels in the intermediate level structure scheme used to describe pyrazine.

A bounded quantum mechanical system, which necessarily has a discrete spectrum, will always display at least almost periodic motion. For such a system a recurrence will eventually reconstruct any chosen initial state.

Kosloff and Rice[7] have discussed an extension of the Kolmogorov entropy, first defined for classical mechanical systems,[8-10] to apply to quantum mechanical systems. The Kolmogorov entropy of a system is an asymptotic measure of its properties; in classical mechanics it is, in principle, computed from an indefinitely long sequence of observations of the time evolution of pairs of trajectories that start from nearby points in phase space. If the initial differences in coordinates and momenta, $\Delta q(0)$ and $\Delta p(0)$, grow rapidly and erratically enough with $|t|$ that prediction and retrodiction of the separation of the trajectories is impossible for lack of sufficiently precise initial conditions, the classical mechanical system is said to exhibit chaos. For a classical mechanical system regular and chaotic motion are characterized by, respectively, zero and nonzero Kolmogorov entropy. The Kosloff–Rice extension of the concept of Kolmogorov entropy to quantum mechanical systems shows that its value is zero for a bounded system since, if the spectrum of the system is discrete, the recurrence time is always finite (although it can be very long). We note that it is also the case in classical mechanics that if the spectrum of the Liouville operator for the system is discrete the Kolmogorov entropy of that system is zero and the motion is regular.[9,10] True relaxation, in the sense of an irreversible approach to some asymptotic state of the system, only occurs when the spectrum of the system is continuous.

As interesting as the preceding argument is from the point of view of formal theory, measures which require extremely long observation periods are usually irrelevant in real experimental situations. It is never possible to

completely isolate a molecule from the rest of the universe. Although the time scale on which small coupling terms generate evolution of a state of the system can be very long, some perturbations, e.g., collisions with a wall or other molecules, greatly restrict the time available for observation of isolated molecule properties. Since a system with a discrete spectrum can exhibit apparent relaxation for some period of time, it is worthwhile examining how the putative characteristics of quantum mechanical chaos are manifest in the time evolution of the system. Note that we have described the time evolution of a system with a discrete spectrum as apparent relaxation since it is really a coherent dephasing and is not irreversible.

Pomphrey[11] has suggested, and others have demonstrated, that the energy level spectrum of a system which is classically chaotic is more regular than is the energy level spectrum of a system which is classically quasiperiodic. The notion underlying this suggestion is that classically chaotic systems have strongly coupled degrees of freedom which, in the quantum mechanical description, implies removal of all degeneracies and "level repulsion." On the other hand, classically quasiperiodic systems have underlying dynamical symmetries which, in the quantum mechanical description, implies the existence of degenerate states. It is the level repulsion mentioned above that tends to regularize the spectrum relative to one which exhibits clustering attributable to degeneracies. We now ask how this difference in the structures of the spectra influences the temporal evolution of a prepared wave packet.

It is worthwhile, before proceeding further, to remark on some features of the relationship between the energy level spectrum of a system and the recurrence time in that system. Consider a situation in which the energy level spectrum has near degeneracies. In this case the recurrence time, neglecting fluctuations, is expected to be very long. We then infer that quantum systems which in the classical limit correspond to quasiperiodic motion have longer recurrence times than do quantum systems for which the corresponding classical motion is chaotic. Furthermore, when the spacing of the levels in the spectrum becomes incommensurate the recurrence time depends on the definition of the precision of the recurrence of the state. For systems with an infinite number of discrete levels a recurrence never occurs even though phase coherence is never lost in the evolution of an initial state. These counterintuitive observations are illustrated by detailed studies of two model systems:

(i) The Jaynes–Cummings[12] model consists of a two level system coupled to a harmonic oscillator. If at $t = 0$ we prepare this system in a coherent state of the oscillator the initial state never recurs and, indeed, has a very complicated partial revival pattern.

(ii) The Wigner–Weisskopf[13] model consists of a single state coupled to an infinite manifold of evenly spaced states. In this system the amplitude of a prepared state decays exponentially for a while. However, if the density of states is finite, after some time there is a partial revival of the initial state amplitude. The partially reconstituted initial stay decays again, and revives at still later times, etc. If the density of states becomes infinite the revival of the initial state is suppressed and the temporal evolution becomes an exponential decay of amplitude.

In each of cases (i) and (ii) the system has zero Kolmogorov entropy because the time evolution is completely predictable.

What emerges from these considerations is that the partial revival time of an initial state can be a more suitable measure of molecular behavior than the recurrence time. We define the partial revival time as the interval required for the initial state to regain a significant fraction of its amplitude. For a large molecule, in which the prepared state is coupled to a dense set of states, the partial revival time can be very long. In principle the partial revival time is of the order of the reciprocal of the largest frequency spacing among the dominant supporting states. Evenly spaced energy level spectra have, therefore, longer partial revival times than do unevenly spaced energy level spectra.

It is worthwhile demonstrating in a different fashion from the argument in Sec. IV B of Ref. 1 that the distribution of energy levels is irrelevant for calculation of the initial decay of the prepared states, i.e., up to the first partial revival time. First consider an initial state which can be represented as an expansion in the eigenfunctions of the system Hamiltonian, i.e.,

$$|\rho\rangle = \sum_n C_n \psi_n. \tag{14}$$

The time evolution of this state is given by

$$|\rho(t)\rangle = \sum_n C_n e^{i\omega_n t}\psi_n, \tag{15}$$

and the amplitude of the initial state is

$$\begin{aligned} f(t) &= \langle\rho(0)|\rho(t)\rangle \\ &= \sum_n |C_n|^2 e^{i\omega_n t}. \end{aligned} \tag{16}$$

Equation (16) can be thought of as a discrete approximation to the Fourier integral

$$F(t) = \int_{-\infty}^{\infty} |C(\omega)|^2 e^{i\omega t} d\omega. \tag{17}$$

If the continuous function $|C(\omega)|^2$ obeys the conditions

$$\begin{aligned} &\int_{-\infty}^{\infty} |C(\omega)|^2 d\omega = 1, \\ &|C(\omega)|^2 \to 0; \quad \omega \to \pm\infty, \end{aligned} \tag{18}$$

there exists a discrete approximation of the type displayed in Eq. (16) for the integral, and when the distance between levels approaches zero the approximation becomes exact, i.e.,

$$f(t) \to F(t). \tag{19}$$

From the point of view of Eqs. (17) and (19) the energy level distribution plays the role of defining the quadrature points of the discrete approximation. In fact if

$$F(t| = \int_{-\infty}^{\infty} g(\omega) d\omega, \tag{20}$$

then

$$f(t) = \sum_n W(\omega_n) g(\omega_n), \tag{21}$$

where the ω_n are the quadrature points, $W(\omega_n)$ are the weight functions and $g(\omega_n)$ is the value of the function g at the quadrature point.

We can now compare the initial decays of two molecules with different energy level distributions. If we assume that the initial state is arbitrary we can choose it in such a way that we obtain the same spectral envelopes $F_1(t) = F_2(t)$ in both molecules. The two spectral distributions, corresponding to the two molecules, will construct different discrete approximations to the same decay integral.

In the following examples we construct the decay patterns for wave packets constructed from several different energy level distributions. Our purpose is to illustrate the varieties of apparent decay and revival of initial state for fully coherent evolution under conditions for which the initial decays are identical.

Consider, first, (a) a uniform distribution of energy levels, (b) energy levels converging to an accumulation point as $(\Delta E)^{-3}$ and (c) a Poisson distribution of energy levels. These spectra are shown in Fig. 1, and the corresponding $f(t)$ in Fig. 2. In these cases the average density of states is the same. Note that the Poisson distribution (c) has the strongest revival pattern since it has relatively large gaps in the spectrum, that distribution (b) has a relatively weak but nontrivial revival pattern and that the uniform energy level distribution (a) has a revival time that coincides with the recurrence time. For the uniform spectrum the recurrence time, in the units shown in Fig. 2, is $2\pi \cdot (40)$, since there are 40 levels in the unit interval.

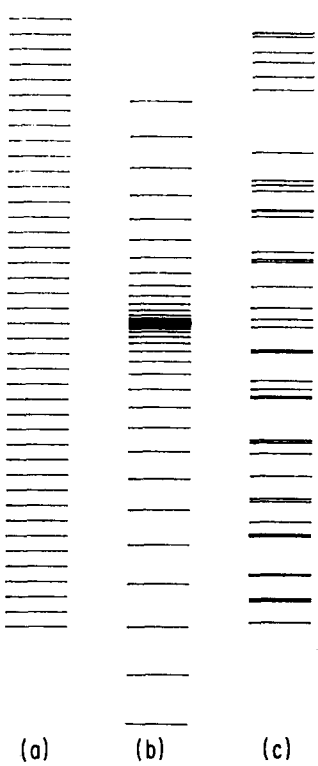

FIG. 1. Model level structures (a) uniform distribution (b) levels converging to an accumulation point as $(\Delta E)^{-3}$ (c) Poisson distribution.

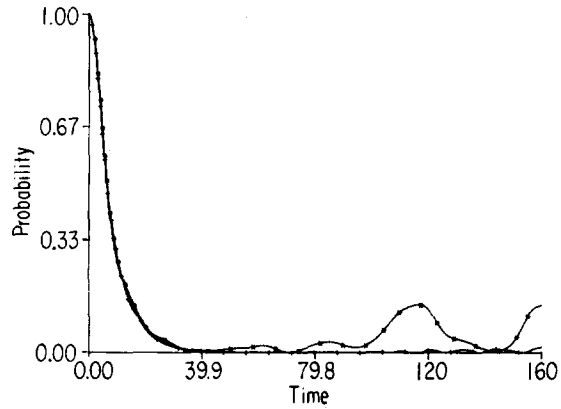

FIG. 2. Evolution of the systems in Fig. 1. — uniform, + cubic, * Poisson.

Consider now spectra modeling those of O_3 and HCN, shown in Fig. 3; the corresponding $f(t)$ are shown in Fig. 4. O_3 has a Wigner distribution of nearest neighbor energy level separations,[14] a characteristic some investigators associate with quantum chaos.[15] The energy levels of HCN tend to stick together because of an underlying dynamical symmetry in the system Hamiltonian.[16] Note that HCN has a strong initial state revival pattern since the spectrum has large gaps; the initial state revival pattern for O_3 is much weaker. The unit of time in the figure for O_3 is 0.02 ps; that for HCN is 0.0069 ps.

It is clear, from these examples, that despite apparent irreversible decay for a time interval, coherent evolution of a wave packet leads to significant but partial revival of the initial state on a time scale short compared to the recurrence time. And, despite the uniform value for the initial rate of decay, the coherence of the wave packet evolution is manifest in the variation of the partial recurrence time, and amplitude, with spectral distribution. Relative to the time scale determined by the initial decay, these partial amplitude revivals occur at very long times. Thus, if evidence for coherence is sought at short times it must be in phenomena other than the partial revival of wave packet amplitude. If the experimental probe does not depend on wave packet coherence, the temporal evolution will appear irreversible on the usual time scale of measurement.

Our point is that what is observed depends on the nature of the experiment. Or, put another way, it is possible to carry out an experiment which does not sample the coherence properties of the system wave function, for which experiment apparent irreversibility is manifest. It is also possible, in principle so long as the system spectrum is discrete, to carry out an experiment which does depend on the coherence properties of the system wave function, for which case partial revivals of

FIG. 3. Level structures for O_3 and HCN.

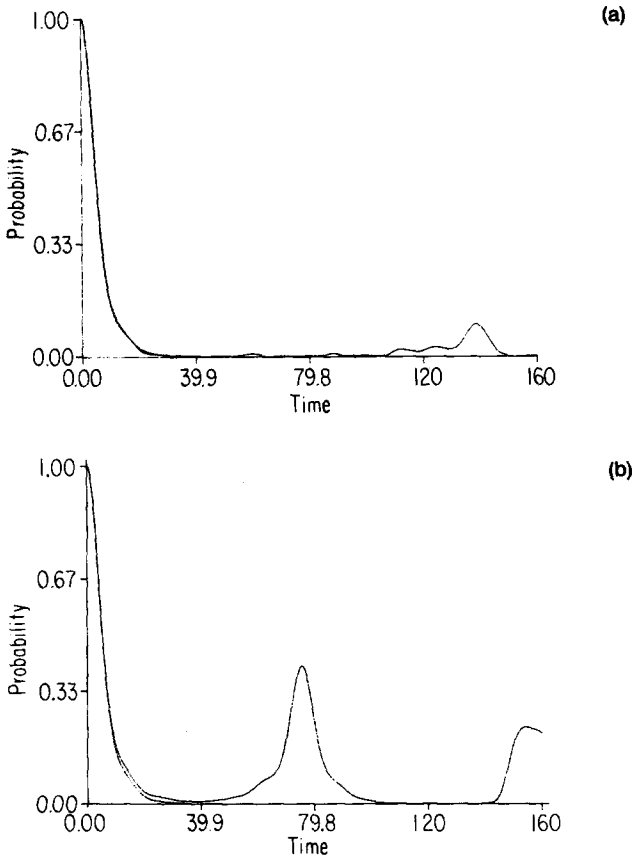

FIG. 4 (a). Evolution of the O_3 system shown in Fig. 3. (b). Evolution of the HCN system shown in Fig. 3.

the initial state or other evidence of phase memory will be found. In addition to the case of pyrazine, which we have discussed, that this is so is illustrated by the experiment of Lambert, Felker, and Zewail.[16] These investigators used picosecond pulses to excite a well defined vibrational mode on the $^1B_{2u}$ surface of anthracene. At the energy of excitation (1420 cm^{-1} of vibrational energy, 30 000 cm^{-1} total energy) there are about 50 $^1B_{2u}$ vibrational levels within the coherence width of the laser, while the total density of (vibrational) states is in excess of $10^9/cm^{-1}$. The emission from the prepared state to the ground electronic state was monitored, with the following results. In the frequency domain the resonance emission is sharp, regular, and can be analyzed in terms of the known normal modes of the molecule. For energies below that of the resonance emission there are clumps of lines in the spectrum. The temporal behavior of the system in the resonance emission region shows recurrences with frequency 1 GHz. In the spectral region where there are clumps of lines recurrences are observed with the same frequency, but phase shifted. Indeed, depending on the emission mode studied there is either a $\pi/2$ phase shift or no phase shift relative to the resonance emission recurrence pattern. Felker and Zewail give a simple and elegant interpretation of these observations in terms of coherent evolution of the prepared state.

Our interpretation of wave packet dynamics in pyrazine, and Felker and Zewail's interpretation of wave packet dynamics in anthracene,[16] can be used to test some of the ideas concerning quantum chaos. We shall focus attention on three of those ideas, namely, the Kosloff–Rice[7] extension of the Kolmogorov entropy theorem to quantum mechanical systems, Heller's criterion[17,18] and the recent definition, by Goelman and Shapiro,[19] of quantum chaos in terms of the properties of the eigenfunction of a stationary state.

As mentioned earlier in this paper, Kosloff and Rice show that the Kolmogorov entropy of a bounded quantum mechanical system is zero, hence there cannot be a quantum chaos with one-to-one relationship with classical mechanical chaos. It is immediately obvious that the observation of coherent wave packet evolution in a region of the spectrum with discrete energy level structure is consistent with the Kosloff–Rice analysis. The examples of wave packet evolution described earlier show how complex the temporal behavior can be given the constraint of phase memory.

Heller's criterion for quantum chaos is conveniently stated in terms of wave packet motion on an energy surface. He proposes that a system is chaotic when, as $t \rightarrow \infty$, the wave packet uniformly covers the available energy surface. In the egalitarian coupling model for intermediate case molecules this condition is achieved. Yet, as we have shown both theoretically and experimentally, the coherence of the system wave function is maintained for all time. Thus, an experiment that does not depend on, or sample, phase coherence will yield a result which agrees with that predicted under the assumption chaos exists, while an experiment that does depend on the coherence properties of the prepared state will yield a result which indicates that the system is not chaotic. It is, then, perhaps a semantic distinction as to whether or not Heller's criterion defines quantum chaos.

Shapiro and Goelman[19] associate quantum chaos with the properties of an eigenfunction and not, as do Kosloff and Rice, with the properties of the spectrum of all eigenfunctions. To be specific, Shapiro and Goelman associate chaos with the condition that the path correlation function

$$P[\psi] = \frac{1}{N} \sum_{i=1}^{N} \psi^*(\mathbf{r}_i)\psi(\mathbf{r}_{i+n}) \tag{22}$$

fluctuates about zero for all $n > 0$. In Eq. (27) $\psi(\mathbf{r})$ is a stationary state wave function and $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$ are a set of cyclically arranged ($\mathbf{r}_{N+n} = \mathbf{r}_n$) ordered points belonging to a self-avoiding space filling path in coordinate space. The conditions that the wave function be normalizable and continuous imply that if the interval between successive points on the path is small enough the path correlation function is nonvanishing. Thus the vanishing of the path correlation function is to be regarded as its limiting behavior for suitable interval between points along the path. Indeed, Shapiro and Goelman show that for the stadium,[19] a system known to be chaotic in its classical mechanical motion for all energies, the path correlation functions of the eigenstates are periodic and nondecaying at low energy whereas this function decays immediately and then fluctuates about zero for all values of n when

the energy is high. The fluctuation of the high energy path correlation function about zero seems to imply there is a random sampling of wave function values, but it must be remembered that this cannot be the case since the wave function satisfies normalization and continuity conditions; the behavior of the path correlation function described is at best pseudorandom. The point to which Shapiro and Goelman draw attention is that wave functions corresponding to slightly different energies are likely to have path correlation functions with oscillations that are not cross correlated. This behavior is consistent with the Kosloff–Rice analysis, which uses properties of the entire spectrum of states to define the Kolmogorov entropy.

Consider how the classical mechanical concept of chaos alters our notion of motion of a representative point in phase space. It has been argued that if the dynamical motion is sufficiently unstable that each open region of the phase space, no matter how small, rapidly spreads to far separated regions of the phase space as time advances, then it is impossible to define the phase space trajectory by considering the motion of smaller and smaller initial regions of the phase space. The statement of impossibility is an extrapolation that contradicts the nature of the solutions of the equations of motion, which require the trajectory to be continuous and differentiable. If, nevertheless, the statement of impossibility is accepted, and on the smallest scale for subdivision of the system phase space the trajectory is not differentiable, the Hamiltonian equations of motion are to be replaced by new equations of motion which account for the "intrinsic randomness" of the system.[20] The consequence of strong instability of motion is, in this view, the breakdown of the deterministic description of dynamics, leading to irreversibility of motion. Note, however, that the stated consequence is ultimately derived from the imputation of behavior of the trajectory that is inconsistent with the Hamiltonian equations of motion.

As already described, the Shapiro–Goelman criterion for quantum chaos exploits the behavior of $P[\psi]$, given by Eq. (22). In the implementation of that criterion it is found that although $P[\psi]$ fluctuates about zero for high energy eigenstates, the amplitude of the fluctuations does not decay as N [see Eq. (22)] increases. Thus, the spatial correlation of ψ does not vanish as N increases. Indeed, we take the behavior of $P[\psi]$ to be descriptive of a very complicated function, but one which has definite phase and amplitude relations everywhere in space. Note that if the fluctuations in $P[\psi]$ were random ψ would be nondifferentiable. Since ψ is an eigenfunction of a bounded Hamiltonian, or in other words a normalizable and continuous solution of the Schröedinger equation, it must also be differentiable. We conclude, then, that $P[\psi]$ can never fluctuate randomly.

The nature of the fluctuations of $P[\psi]$ is relevant to the interpretation of wave packet dynamics in pyrazine and anthracene. In both cases the stationary state wave functions, at the energies of excitation, must be very complicated in the sense of having many nodes and highly patterned spatial distributions of amplitude. That this is so follows from the observation that, at the energy considered, if such a stationary state wave function is represented as a mixture of vibrational functions drawn from the coupled electronic surfaces, those vibrational wave functions must correspond to reasonable excitation and have many nodes. Accordingly, it is reasonable to expect a computation of $P[\psi]$ for such eigenfunctions to fluctuate about zero. But, as we have already argued, the existence of such fluctuations does not imply that phase memory is lost, and the experiments we have described show that it has not been lost, i.e., ψ still has definite phase and amplitude relations everywhere in the bounded space.

Briefly put, if an experiment is designed to probe for coherence in the evolution of a prepared state in a quantum mechanical system with discrete spectrum, it will be found that coherence triumphs over chaos.

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