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MOLECULAR BEHAVIOR IN THE QUASI-PERIODIC AND STOCHASTIC REGIMES*

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INTRODUCTION

Nonlinear dynamics has been applied to chemistry in a variety of ways, for example, in the analysis of spatial and temporal oscillations in chemical reactions. The equations for the reaction rate at various regions of space are nonlinear in such cases. Several other papers in this volume touch upon this subject. Nonlinear dynamics has also been used to treat collisions between molecules by solving Hamilton's equations for their motion. Many recent experimental data that have become available on collisions and reaction dynamics have been treated in this way.

In earlier years, dynamical information about chemical reactions was obtained only from chemical reaction rates and their dependence on temperature. Particularly since the early 1960s, the introduction of new technology, such as molecular beams and lasers, has permitted researchers to acquire much more detailed dynamical information on reactive and nonreactive collisions, information such as quantum state–to–quantum state chemistry in some instances and the measurement of the distribution of final vibrational-rotational-translational quantum states in others, as well as various degrees of averaging of similar information. The theoretical studies in the field of collisions have been classical, semiclassical, and quantum in nature.

Information has also become available on topics related to vibrational energy redistribution within a molecule, from, e.g., studies of unimolecular reactions, chemical activation, infrared multiphoton dissociation of molecules, and widths of high overtone spectra of local vibrational modes in molecules. (Some references are given in Reference 1.) The detailed interpretation of many of these cases is still being resolved; the entire field of intramolecular relaxation is a particularly active one at this time. One expects that the isolated molecule will behave largely "ergodically" at high enough vibrational energies, reaching most parts of the vibrational phase space available at those energies. A statistical theory of unimolecular reactions, RRKM, which assumes this form of behavior, is commonly used for treating high vibrational energy data. One current interpretation of the infrared multiphoton absorption of energy by molecules is that initially, at low vibrational energies, the molecule does not behave "ergodically," but rather absorbs the laser infrared radiation coherently; at higher vibrational energies, it does behave "ergodically." In the case of high overtone spectra of local modes, it is not yet known whether the spectral width is due to an energy loss to the other modes or to a "vibrational dephasing"; each arises from anharmonic coupling with the other modes.

We consider below, in the application of nonlinear dynamics to chemistry, the

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problem of the intramolecular behavior of molecules both classically and quantum mechanically.

The classical Hamiltonian for the motion of atoms in a molecule has much in common with those extensively investigated in the literature of astronomy and related subjects. Thus, the results in astronomy have implications for the chemical problems. For example, the largely quasi-periodic behavior found in numerical experiments for the former at low energies and the largely stochastic ("chaotic"), but still deterministic, behavior found at high energies is expected to prevail for classical mechanical molecules, too. While molecules obey quantum mechanical laws rather than classical, the quantum behavior should be reasonably similar to the classical at high enough energies. Nevertheless, the role played by quantum restrictions is an important one and must be included in estimates for the onset of "stochastic" behavior in a molecule.

In the present paper, we indicate how classical results in the quasi-periodic regime provide direct information about the corresponding quantum mechanical behavior when semiclassical methods are introduced. While the corresponding treatment for the stochastic regime in quantum mechanics is much less developed, a criterion for conditions under which a quantum stochastic regime occurs will be proposed. A criterion for quantum stochasticity is of interest, since, in some experiments, the behavior of a molecule can differ, depending upon which regime it is in.[1]

Quasi-Periodic Regime

Einstein pointed out that a system can be quantized for the quasi-periodic regime by finding the N independent canonical invariants $\oint \mathbf{p} \cdot \mathbf{dr}$ (N for N degrees of freedom) and setting them equal to $n_i h$, or nowadays $(n_i + \frac{1}{2})h$ for an oscillator, where $n_1, \ldots n_N$ are sets of integers.[2] The KAM theorem ensures that invariant tori, and with them these action integrals, exist in the phase space for almost all initial conditions if the perturbation from an integrable system is sufficiently small.[3] Using such concepts on quantization, derived now from multidimensional semiclassical arguments,[4,5] good agreement has been obtained with eigenvalues calculated quantum mechanically from a large variational basis set.[6-9] Semiclassical eigenvalues were calculated for the first time for systems with smoothly varying potentials by integrating Hamilton's equations of motion,[6] using a familiar Hamiltonian,[10]

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x(y^2 + \eta x^2), \qquad (1)$$

with coordinates x and y, momenta p_x and p_y, and with ω_x and ω_y incommensurable. A typical classical trajectory obtained in this way is given in FIGURE 1. On the "ellipse," the potential energy equals the total energy. The trajectory must lie within this boundary, but it clearly occupies a much more confined region. Within the region $ABCD$, the corresponding quantum mechanical wave function is large and oscillatory, while, outside it, it dies away exponentially with distance.[4,5] The boundary lines AB, BC, CD, and DA serve as caustics for the wave function. By calculating $\oint \mathbf{p} \cdot \mathbf{dr}$ along the curve AB and back and along the curve BC and back, setting them equal to $(n_x + \frac{1}{2})h$ and $(n_y + \frac{1}{2})h$, respectively, and adjusting the initial conditions and, thereby, the energy E so that n_x and n_y were integers, semiclassical eigenvalues were calculated.[6] They agreed well with the quantum mechanical eigenvalues.

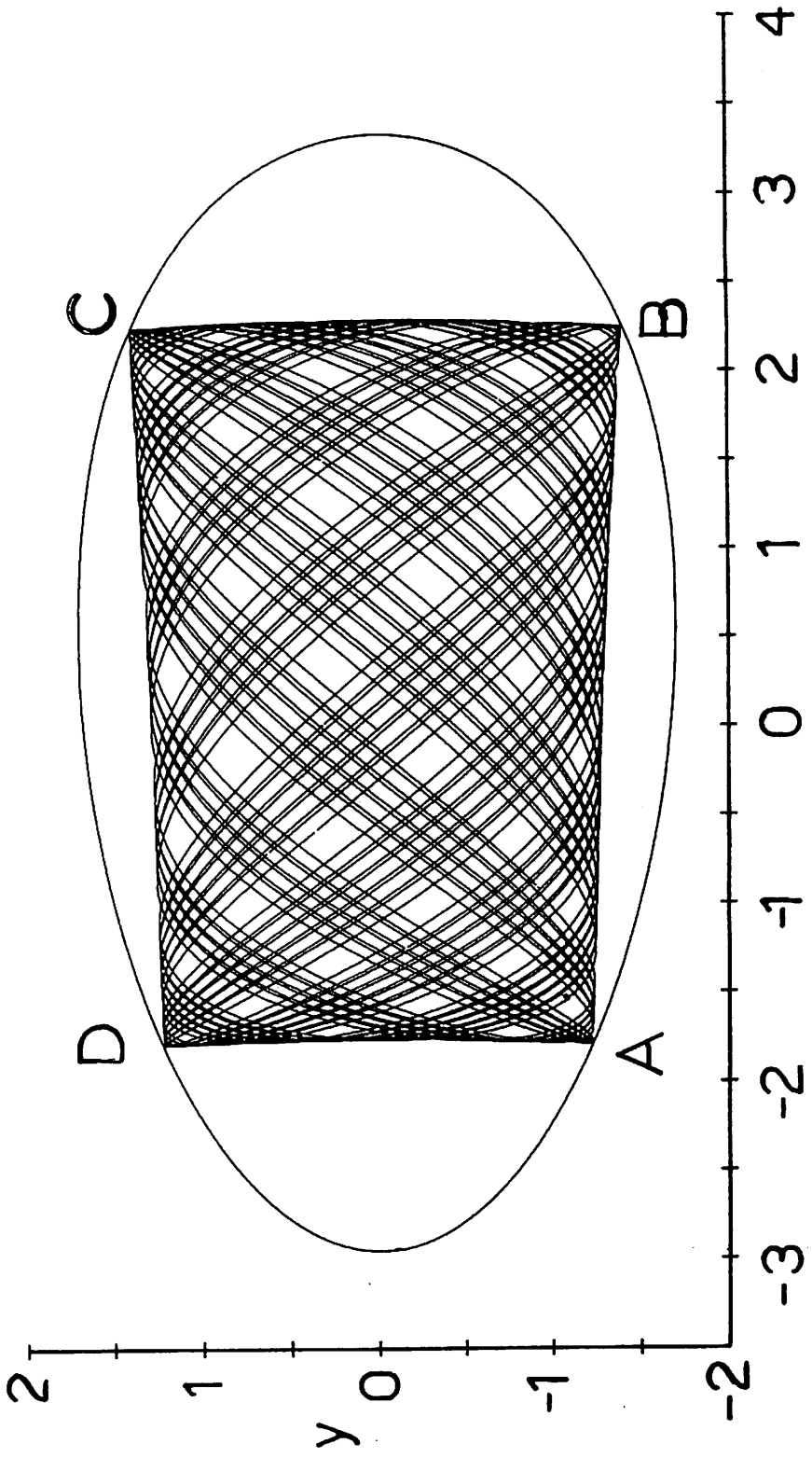

FIGURE 1. A trajectory for the Hamiltonian (1) with ω_x and ω_y incommensurable.

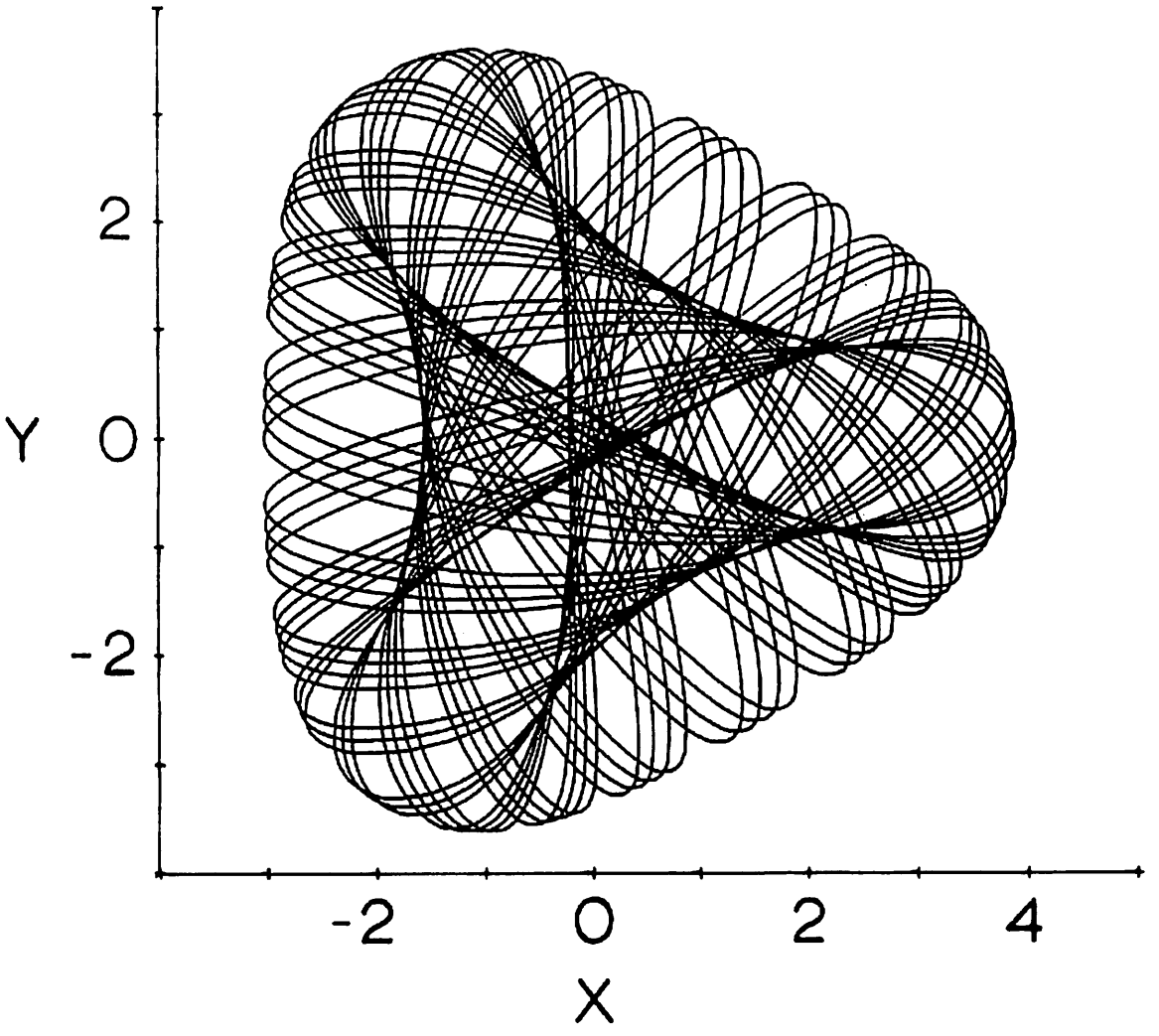

FIGURE 2. A trajectory for the Hamiltonian (1) with $\omega_x = \omega_y$.

A second method was then found by using the trajectory to generate two Poincaré surfaces of section: a plot of p_x versus x at $y = 0$ and $p_y > 0$, and a plot of p_y versus y at $x = 0$ and $p_x > 0$.[7] Each of these consisted of a series of dots on an ellipse-like figure. The area of each figure can readily be evaluated, and equals the corresponding value of $\oint \mathbf{p} \cdot d\mathbf{r}$ for that trajectory. The initial conditions were chosen so that the areas were $(n_x + \frac{1}{2})h$ and $(n_y + \frac{1}{2})h$, respectively, where n_x and n_y are integers. Once again, good agreement between quantum mechanical and semiclassical eigenvalues was obtained.[7]

Perturbative and perturbative-iterative methods were subsequently developed.[11-17] They provide a useful complement to the trajectory method described above; they can be computationally fast when the integrals can be evaluated analytically, but can break down (do not converge) when the distortion of the tori is large enough, under conditions where the trajectory method can still be used.

The trajectory method[18] has also been used to treat systems where ω_x and ω_y are commensurable,[8,9] e.g., when they are 1:1 and when they are 2:1 (Fermi resonance). In these cases, the trajectory patterns were no longer box-like, as in FIGURE 1, but tended rather to be circular in the 1:1 case (FIGURE 2) and parabolic in the 2:1 case (FIGURE

3), reflecting extensive energy exchange between the x and y degrees of freedom.[8,9] For these systems, the idea of a curvilinear surface of section was introduced by employing polar coordinates (r, θ) for the 1:1 case and plotting p_r versus r at some θ ($p_\theta > 0$) and p_θ versus θ at some r ($p_r > 0$).[8] Once again, areas were evaluated and eigenvalues were obtained, the quantization procedure having allowed for the caustics touched by the trajectory.[8]

Similarly for the ω_x:ω_y = 2:1 case, parabolic coordinates (ξ, η) were introduced, curvilinear surfaces of section, e.g., p_ξ vs ξ at constant η and $p_\eta > 0$, were plotted, the areas were evaluated, and, thereby, the eigenvalues were obtained.[9] The trajectories consisted of three types, those shown in FIGURE 3, those curved in the opposite sense, and trajectories representing a transition between the two (e.g., Figure 10 of Reference 9), in which the trajectory passes through a focus in addition to touching the caustics. In each case, allowance for the effect on the phase of the semiclassical

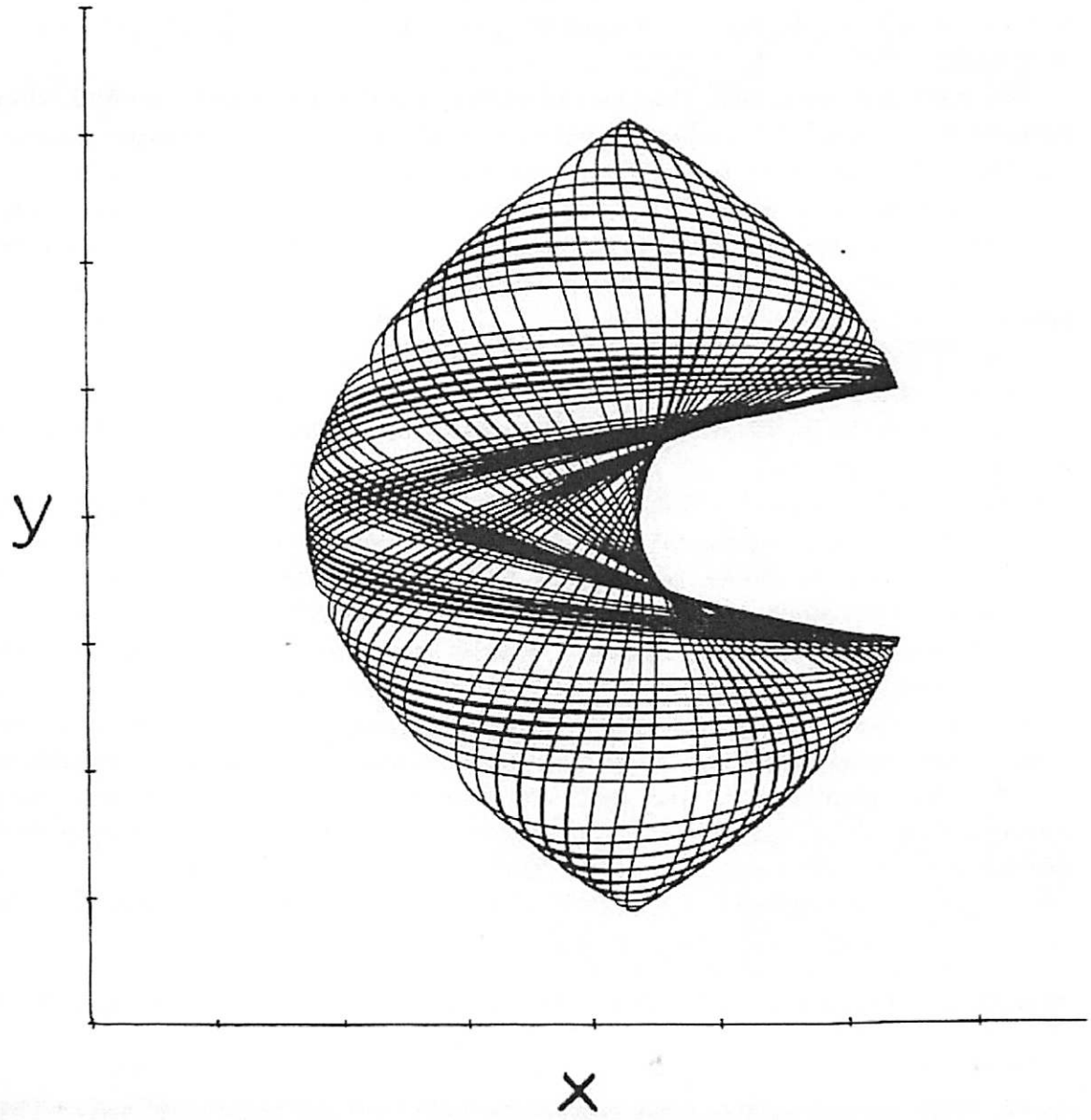

FIGURE 3. A trajectory for the Hamiltonian (1) with $\omega_x = 2\omega_y$.

wave function of a trajectory touching a caustic or passing through a focus was made.[4]

Recently, eigenvalues have been obtained quantum mechanically for a Hamiltonian whose classical version is given by equation 2 (cf. equation 1.7 and Figure 2 of Reference 19),[19]

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + x^2 + y^2) + x^4 + 2cx^2y^2 + y^4. \quad (2)$$

The system becomes degenerate, and also separable and, hence, integrable, at $c = 0$, 1, and 3. Thereby, plots of the energy eigenvalues versus c show actual crossings. Systems near these crossings have much in common with the nearly degenerate (1:1 and 2:1) systems mentioned above and so can presumably be treated by the Poincaré surface of section method in the quasi-periodic regime.

The surface of section method has recently been extended from two to three dimensions.[20] The perturbative and perturbative-iterative methods are readily applied to three dimensions, as well as two, and applications to actual molecules (H_2O, OCS) with added approximations, e.g., neglect or separate treatment of Coriolis forces, have been made.[13,15,16]

We have not mentioned, thus far, an earlier method, one which quantizes only periodic trajectories.[21,22] This method would be applicable to fully degenerate systems, but has been shown to lead to spurious eigenvalues in other applications.[7] A modification has been given,[23] based on an expansion about the periodic trajectory, and represents an approximation to the trajectory method of References 6–9. Periodic trajectories have been used to obtain useful information about the density of states.[24,25]

The surface of section method has also been recently applied to a resonant scattering system to locate the positions of the scattering resonances.[26] It yielded good agreement with the quantum mechanical results.[27] Interestingly enough, resonances in the system studied that were not located accurately in the quantum mechancal calculations corresponded classically to trajectories that were not quasi-periodic.[26] They displayed a thin stochastic layer behavior that permitted them to escape.

A rapid way to obtain information from a trajectory about differences of eigenvalues in the quasi-periodic regime has also been found, namely to calculate an autocorrelation function and, thence, a Fourier transform.[28] Several spectral lines were obtained. Their positions agreed well with quantum mechanical lines calculated variationally from a large basis set.[28] Because the positions of the lines vary only slightly with initial conditions in the quasi-periodic energy regime, it was possible to use, for the calculation of the spectrum from the trajectory, initial conditions corresponding to appropriate zeroth order values for the action variables. The spectral method has been subsequently used in other investigations;[29,30] Noid et al. recently have applied it to molecules such as OCS with Coriolis and other terms present in the Hamiltonian,[31] and it has also been used to calculate intensities.[32]

Stochastic Regime

In the stochastic regime, most trajectories yield Poincaré surfaces of section that resemble shotgun patterns.[33] The patterns sometimes tend to avoid certain areas, those which are pre-empted by those invariant tori which remain even in the high energy

regime. For example, in the Hénon-Heiles Hamiltonian system, namely, equation 1 with $\omega_x = \omega_y$ and $\eta = -1/3$, there are, at the highest energies, preserved tori corresponding to high "angular momentum" in the xy plane in FIGURE 2. It was possible to quantize those tori semiclassically using the Poincaré surface of section method described in the preceding section.[8,34]

In the case of the destroyed tori region, two methods have been suggested for computing the energy eigenvalues in this stochastic regime. One is to note that the tori persist in perturbation theory even when they do not in the actual system and to quantize these perturbatively-calculated tori.[14,17] A second method is to calculate the

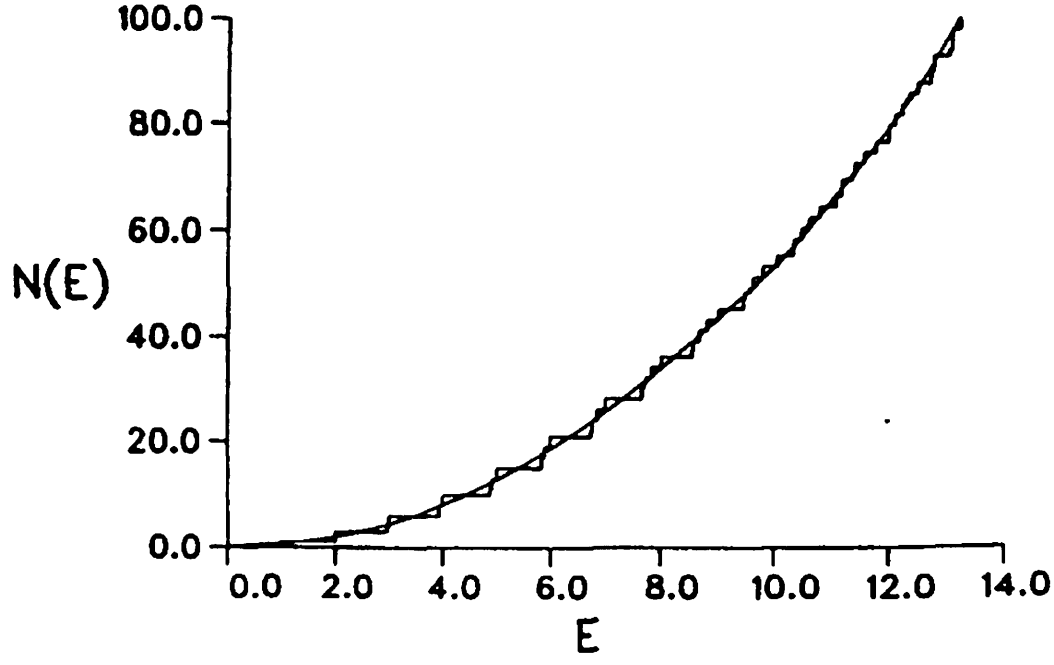

FIGURE 4. A plot of both the classical and the quantum number of states versus energy for the Hénon-Heiles system with $\lambda = 0.11180$ (Reference 32).

classical number of states as a function of energy using a microcanonical ensemble,[32]

$$N_{cl}(E) = \int \theta(E - H) \prod_{i=1}^{N} \frac{dq_i dp_i}{h}, \tag{3}$$

for a system with N degrees of freedom. Here, θ is the unit step function. $N_{cl}(E)$ is a smooth function, while the quantum mechanical function rises in steps at each eigenvalue, as shown in FIGURE 4. For the system studied, equation 3 located the quantum states to an accuracy of about one state.[32] The first method yielded good results.[14] It does leave uncertain the order of perturbation to be used, unless some form of convergence can be proved, and may encounter difficulties such as that described in FIGURE 6.

In a recent study of the quantum mechanical energy levels of the Hénon-Heiles system, a surprising result was obtained: the sequence of the energy levels (levels characterized by principal and pseudo angular momentum quantum numbers, n and l, respectively) in the classically quasi-periodic regime continued smoothly into the

TABLE 1

DIFFERENCES OF EIGENVALUES FOR VARIOUS SEQUENCES

Transition				Transition			
$n\ l$	→	$n\ l$	ΔE	$n\ l$	→	$n\ l$	ΔE
Low l				Intermediate l			
(6,0)		(7,1)	0.92	(4,0)		(5,1)	0.95
(7,1)		(8,0)	0.89	(5,1)		(6,2)	0.94
(8,0)		(9,1)	0.89	(6,2)		(7,3)	0.95
(9,1)		(10,0)	0.87	(7,3)		(8,4)	0.96
(10,0)		(11,1)	0.84	(8,4)		(9,5)	0.95
(11,1)		(12,0)	0.82	(9,5)		(10,6)	0.95
(12,0)		(13,1)	0.79	(10,6)		(11,7)	0.95
				(11,7)		(12,8)	0.95
			High l				
(1,1)		(2,2)	1.00	(7,7)		(8,8)	1.01
(2,2)		(3,3)	1.00	(8,8)		(9,9)	1.01
(3,3)		(4,4)	1.01	(9,9)		(10,10)	1.01
(4,4)		(5,5)	1.01	(10,10)		(11,11)	1.02
(5,5)		(6,6)	1.01	(11,11)		(12,12)	1.01

NOTE: The energy levels of the (7, ±3), (10, ±6), (3, ±3), (6 ±6), (9, ±9), and (12, ±12) states are split. The transitions involve the means for the ±l states, and so introduce uncertainties in the relevant ΔE column of ±0.02, ±0.01, ±0.00, and ±0.005, respectively, whenever these states are involved. For notational brevity, the ± symbol is omitted in the value of l in the table. This table is taken from Reference 32.

classically stochastic regime.[32] Examples of these sequences were those for low angular momentum $(n, \pm 1)$ to $(n + 1, 0)$ and $(n, 0)$ to $(n + 1, \pm 1)$ for odd and even n, respectively, those of intermediate angular momentum $(n, \pm[n - 4])$ to $(n + 1, \pm[n - 3])$, and those of high angular momenta $(n, \pm n)$ to $(n + 1, \pm[n + 1])$ (TABLE 1). This result of regular eigenvalue sequences was expected for the high l $(= n)$ region, since semiclassically such quantum states corresponded to invariant tori even in the classically largely "stochastic" regime, but it was surprising for the low and intermediate ls: these states correspond semiclassically, at high energies, to destroyed tori. If one assumes that regular sequences of eigenvalues indicate that the relevant eigenfunctions are not "statistical" in character, i.e., not quantum mechanically "stochastic," then one concludes that nonstochastic quantum mechanical states occur, even in an energy regime that is classically largely stochastic. That is, classical stochasticity does not imply quantum stochasticity. To further develop an understanding of this possibility is an aim of this paper. We have commented elsewhere on the relation of "stochastic" wavefunctions to the problems mentioned in the Introduction.[1]

A statistical ("stochastic") wavefunction is described as one that yields averages for dynamical quantities that are approximately equal to their microcanonical averages at that energy: when the states are sufficiently dense, a "microcanonical" average can be computed by averaging over all quantum states in a small interval $(E, E + \delta E)$. For large enough quantum numbers, the classical microcanonical average could also be used for comparison. A nonstatistical wavefunction corresponds semiclassically to an invariant torus when the latter exists, and would yield, instead, an average approximately equal to the classical average over that torus.

A statistical wavefunction could arise in the following way. We assume (but shall need to test this in later work) that, in the absence of avoided crossings, the principal effect of the perturbation λ is to distort the shape and extent of the region largely occupied by the wavefunction (the shaded regions in FIGURES 1 to 3), but not to otherwise change it drastically. In that case, if one plots the eivenvalues versus some perturbation parameter (e.g., λ in equation 1) and there is no avoided crossing, then each state would have a nonstatistical eigenfunction. If, however, two such eigenvalues approach each other and then repel as the perturbation parameter is increased, one has an avoided crossing (FIGURE 5).† Such an avoided crossing of two energy levels

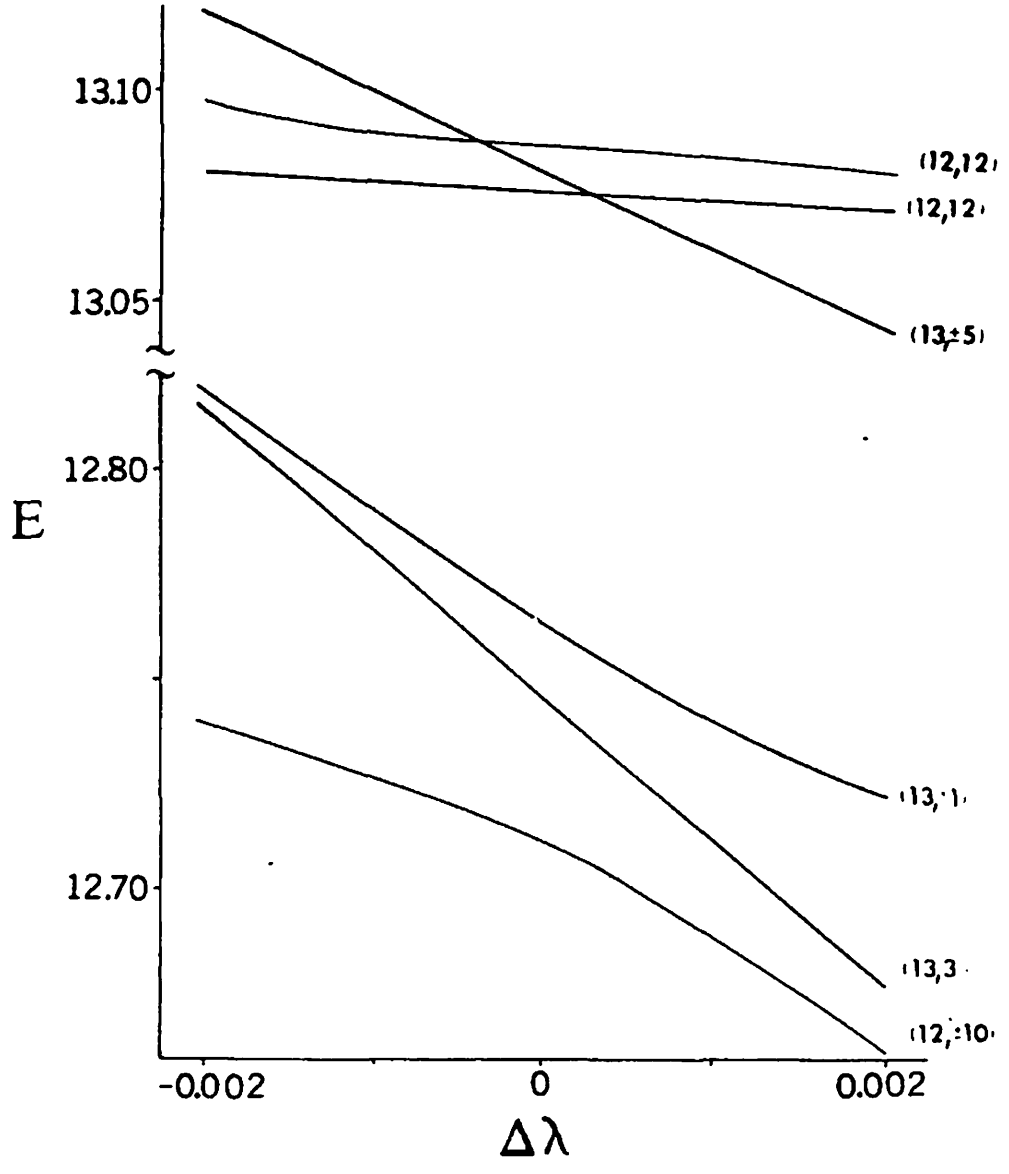

FIGURE 5. An example of an avoided crossing of two pairs of quantum states of the same symmetry, (13, ±1), (12, ±10), in a plot of eigenvalue E versus changes in a parameter λ for the Hénon-Heiles system, taken from Reference 32. Also given is an actual crossing of states (12, ±12) (split) with (13, ±5)—an allowed crossing, since these two pairs of states are of different symmetry.

†To be sure, there is no sharp line differentiating such avoided crossings from more distant ones; only the former is relatively important in the mixing process.

does not yet convey a statistical character on each of the two wavefunctions. Rather, in the vicinity of the avoided crossing, each wavefunction has some of the characteristics of the two wavefunctions that would have arisen had the avoided crossing not occurred.[1,32] An avoided crossing is an analogue of an isolated classical resonance: a vibrational frequency, which corresponds semiclassically to a difference of eigenvalues, becomes nearly zero in the vicinity of the avoided crossing, as it does in the classical case. In the Hénon-Heiles system for the range of parameters studied in

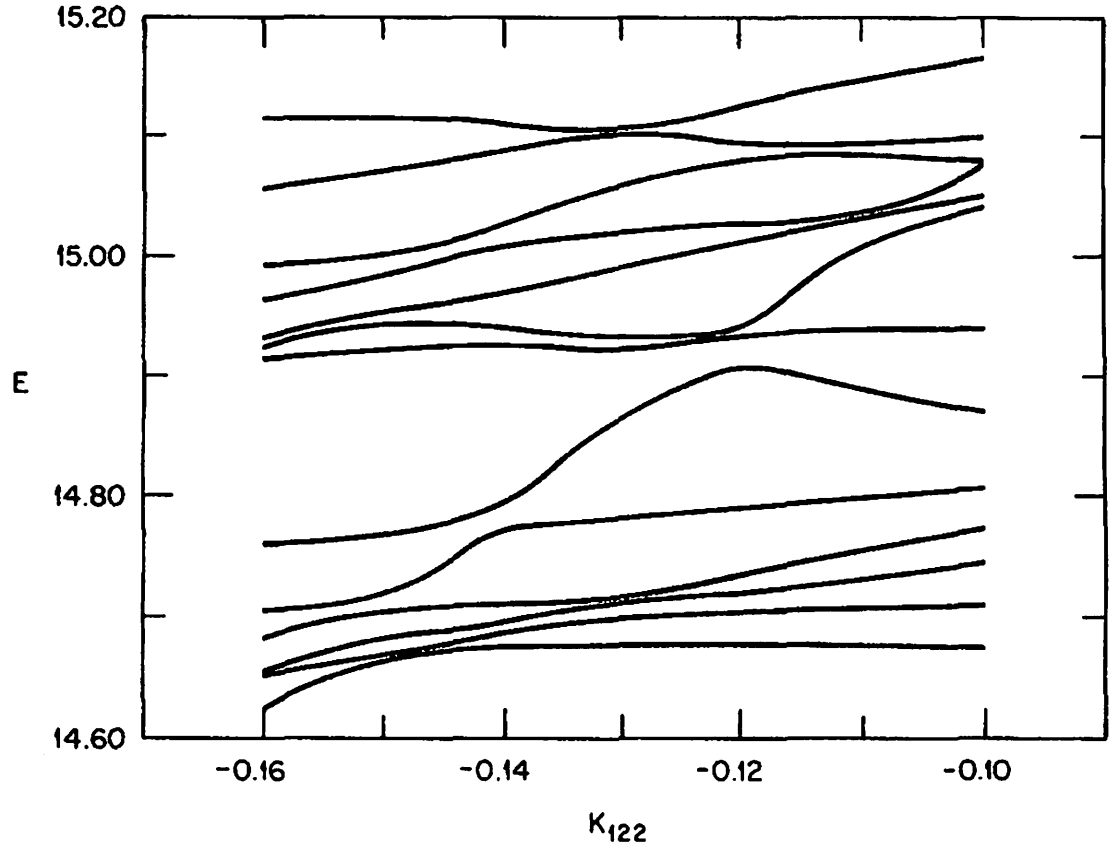

FIGURE 6. An example of overlapping avoided crossings. A plot of eigenvalues versus a parameter k_{122} in the Hamiltonian H,

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$$
$$+ k_{122}xy^2 + k_{133}xz^2 + k_{233}yz^2 + k_{111}x^3 + k_{222}y^3 + k_{1122}x^2y^2 + k_{2233}y^2z^2,$$

where $\omega_x:\omega_y:\omega_z = 2:1:1$. Only eigenvalues for eigenfunctions even in y are plotted. The absence of hidden symmetries (producing actual crossings) was assumed in joining the points (not shown).

Reference 2, we found, in fact, only one avoided crossing (FIGURE 5) and 99 bound states for the value of the parameter λ used in equation 1, so the regular sequences we observed for the eigenvalues become more understandable.

A way of obtaining a statistical wavefunction is to have many "overlapping avoided crossings,"[32] an analogue of overlapping resonances in the classical case. We are now making a number of quantum mechanical studies of this behavior for various systems,[35,36] with a view toward distinguishing isolated avoided crossings from

overlapping ones and examining the behavior of the corresponding wavefunctions. Nondegenerate perturbative methods are not expected to accurately calculate the eigenvalues involved in overlapping avoided crossings (i.e., not better than the "splitting"). Thus, the real test for any method that aims to calculate semiclassical eigenvalues in the stochastic regime is a system involving many overlapping avoided crossings. An example of such a system is given in FIGURE 6.[36]

One treatment of overlapping resonances for classical systems is Chirikov's.[37] It appears to be less applicable, or less readily applied, to the Hénon-Heiles system than to some others; however, it serves as a vehicle for seeing how the onset of classical stochasticity implies quantum stochasticity only when additional criteria are also fulfilled. We first briefly recall some of its features, in order to place a proposed criterion for the onset of quantum stochasticity in context.

The Hamiltonian in action-angle variables (J, w) is written as

$$H(J, w) = H_0(J) + \epsilon \sum_n V_n(J) e^{2\pi i n \cdot w}, \tag{4}$$

after expressing the term $V(J, w)$ in terms of its Fourier components. H_0 is the integrable part of H. J, n, and w are collective variables denoting $J_1, \ldots J_N$, $n_1, \ldots n_N$, and $w_1, \ldots w_N$, and $n \cdot w$ represents $\Sigma_i n_i w_i$. Since H is real, V_n equals V^*_{-n}.

A resonance occurs when there is some value of J, J^r, such that there is a commensurability among the ω_is (J^r denotes $J^r_1, \ldots J^r_N$):

$$m \cdot \omega(J^r) \equiv \sum_i m_i \omega_i(J^r) = 0 \tag{5}$$

The resonance is an isolated resonance when one need consider only one set of integers m_i for which (5) holds. In this case, one also recalls that the Hamiltonian (4) is integrable (even when multiples of m are included); a canonical transformation to new variables (I, $\bar{w}$) is introduced such that $\Sigma m_i w_i$ equals a new angle variable $\bar{w}_1$, e.g., via a generating function $S(I, w)$,

$$S = I_1(m \cdot w) + I_2(\cdots) + \cdots I_N(\cdots). \tag{6}$$

The $(\cdots)$ symbols denote other linear combinations of the ws. If the new angle variables are denoted by $\bar{w}_i$, then J_i equals $\partial S/\partial w_i$ and $\bar{w}_i$ equals $\partial S/\partial I_i$, whence

$$\bar{w}_1 = \sum_i m_i w_i. \tag{7}$$

H then becomes a function of the Is and of this single $\bar{w}_1$ variable. All the Is except I_1 are constants and so are good action variables ($\dot{I}_i = \partial H/\partial \bar{w}_i = 0, i \neq 1$). By equating H with E, I_1 is expressed in terms of I and $\bar{w}_1$. Defining a new action variable, $\bar{I}_1 = \oint I_1 \, d\bar{w}_1$, N action variables have been defined and are constants of the motion, and so the Hamiltonian is integrable.

To formulate and illustrate a quantum mechanical analogue of an isolated resonance, we consider only the $n = m$ term in (4). H can be written in terms of $\cos 2\pi \bar{w}_1$, since any $\sin 2\pi \bar{w}_1$ can be incorporated in a cosine term by redefining the zero of $\bar{w}_1$. The coefficient of this term will be denoted by $\epsilon V_m(I)$. The value of I, i.e., of $I_1, \ldots I_N$, at the resonance (5) is denoted by I^r. Because of the smallness of ϵ, one can

approximate this I-dependent $V_m(I)$ by $V_m(I')$. The $H_0(J(I))$ will be written simply as $H_0(I)$ for notational brevity, and (5) now becomes

$$H = H_0(I) + \epsilon V_m \cos 2\pi \overline{w}_1. \tag{8}$$

A frequency Ω_i is defined as $\partial H_0/\partial I_i$, where Ω_1 is

$$\Omega_1 = \frac{\partial H_0}{\partial I_1} = \sum \left(\frac{\partial H_0}{\partial J_i}\right)\left(\frac{\partial J_i}{\partial I_1}\right) = \sum_i m_i \omega_i, \tag{9}$$

on noting that $\partial J_i/\partial I_1 = \partial^2 S/\partial w_i \partial I_1$ and using (6). From (5), Ω_1 vanishes at $I_1 = I_1', \ldots I_N = I_N'$.

If H_0 is expanded in powers of $I_1 - I_1'$, retaining terms up to the second power, one has

$$\begin{aligned} H \simeq\ & H_0(I_1', I_2, \ldots I_N) + \Omega_1^{(1)}(I_1 - I_1') + \tfrac{1}{2}\Omega_1'^{(1)}(I_1 - I_1')^2 \\ & + \epsilon V_m \cos 2\pi \overline{w}_1 = E, \end{aligned} \tag{10}$$

where $\Omega_1^{(1)}$ and $\Omega_1'^{(1)}$ denote Ω_1 and $d\Omega_1/dI_1$, each evaluated at $I_1', I_2, \ldots I_N$. $\Omega_1^{(1)}$ vanishes at $I_1', I_2', \ldots I_n'$. To the extent that it depends on the I_is and that I_i departs from I_i' $(i \neq 1)$, the Ω_1 in (10) will be nonzero and the resonance may be destroyed. However, this effect is frequently neglected and one can then write H as

$$H \simeq H_0(I_1', I_2, \ldots I_N) + \tfrac{1}{2}\Omega_1'^{(1)}(I_1 - I_1')^2 + \epsilon V_m \cos 2\pi \overline{w}_1 = E, \tag{11}$$

where $\Omega_1'^{(1)}$ is evaluated at $I_1', \ldots I_N'$. If $H_0 + |\epsilon V_m| - E > 0$, then the variable $2\pi \overline{w}_1$ is confined to an interval less than 2π, and, thereby, the motion of the w_is is highly "correlated." At $H_0 + |\epsilon V_m| - E = 0$, I_1 fluctuates during the motion by an amount $\Delta I_1'$, the width of the Chirikov resonance,

$$\Delta I_1' \simeq 2\left(\frac{\epsilon V_m}{\Omega_1'^{(1)}}\right)^{1/2}. \tag{12}$$

This region lies between the two hyperplanes, $I_1 = I_1' - \tfrac{1}{2}\Delta I_1'$ and $I_1 = I_1' + \tfrac{1}{2}\Delta I_1'$, in J-space. At any energy, the resonant region in J-space is the intersection of the energy shell with the laminar region, and so occupies an $(N-1)$-dimensional volume. The resonant region increases in size with increasing energy, since V_m typically increases with increasing values of the Js. Its extension in J-space is, at any energy, really somewhat more limited than is indicated by (12), since $\Omega_1^{(1)}$ may depart from zero when one or more of the $I_2 - I_2', \ldots, I_N - I_N'$ becomes appreciable in magnitude.

If there is some other resonance, e.g., for other integers m',

$$\sum_i m_i' \omega_i' = 0 \tag{13}$$

at some point $J = J''$, one can make a similar treatment, define a new I_1' related to the new integers $(\partial J_i/\partial I_1' = m_i')$, and obtain a resonance width $\Delta I_1''$. These two resonant regions are quantum mechanically significant only when they contain at least one quantum state, i.e., when $\Delta I_1'/h > 1$ and $\Delta I_1''/h > 1$.

The onset of stochasticity begins when two or more such resonance regions overlap. At some energy E, let the overlap volume, an $(N-1)$-dimensional phase space volume, be $v(E)$, calculated by means of the above considerations. For the onset of

quantum mechanical stochasticity we require that there be at least several quantum states in $\upsilon(E)$, and so, in order of magnitude, that

$$\frac{\upsilon(E)}{\hbar^{N-1}} > 1 \tag{14}$$

in order that there be a near statistical character to the wavefunctions of each of these quantum states. We also require that the point $I = I'$ be reasonably close to a quantum state, so that the difference between I' and the value of I for the nearest quantum state I^{qs} should be such that the resonance is not destroyed at that quantum state, e.g., roughly, for the given $I'_2, \ldots I'_N$, that

$$|I'_1 - I_1^{qs}|\Omega_1'^{(1)} < |\epsilon V_m|. \tag{15}$$

Tests of the validity of conditions for quantum stochasticity are now in progress. Other views of quantum stochasticity have also been proposed.[38]

An approximate quantum mechanical version of equation 10 is obtained by replacing each J_i by $(\hbar/i)\partial/\partial w_i$ or, better, by this quantity plus $\delta_i h$, where δ_i depends on the nature of the i'th degree of freedom;[39] δ_i is $\frac{1}{2}$ for an oscillator. The existence of the cosine term in (12) causes, in a two-state approximation, an avoided crossing when $\Omega_1 \simeq 0$, if the quantum numbers corresponding to $J_1, J_2, \ldots J_N$ for the two states differ by $m_1, m_2, \ldots m_N$. This analogue of an isolated classical resonance can also involve the coupling of more than two states at a time, each differing from the next by the changes in quantum numbers, $\Delta n_1, \ldots \Delta n_N$, equal to $m_1, \ldots m_N$, rather than only two quantum states. In a sense, therefore, if V_m is large enough, it can cause a "local" quantum mechanical stochasticity. If V_m is small enough, it will only mix two eigenstates at a time.

Summary

We illustrated how some of the results in nonlinear classical dynamics, particularly those in the quasi-periodic regime, can be related to quantum mechanical results. Evidence that classical "stochasticity" does not imply "quantum stochasticity" was given, and a relation of quantum mechanical stochasticity to overlapping avoided crossings was proposed. A possible condition for the occurrence of quantum stochasticity was suggested and is now being tested, using a criterion for quantum stochasticity.

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