Properties of vibrational energy levels in the quasiperiodic and stochastic regimes[a),b)]

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Several aspects of the quantal energy spectrum are explored for the Henon–Heiles Hamiltonian system: a striking and initially unexpected continuation of sequences of eigenvalues from the quasiperiodic to the stochastic regime, the origin of large second differences $\Delta^2 E_i$ of eigenvalues arising from variation of a parameter, the comparison of classical and quantal spectra, and a comparison of the "classical" and quantal number of states. In the study of the second differences we find both "crossings" and "avoided crossings" of the eigenvalues. We discuss the importance of overlapping avoided crossings as a basis for a possible theory of "quantum stochasticity".

I. INTRODUCTION

The classical motion of nonlinearly coupled oscillators tends to be predominantly "quasiperiodic," or "regular," at low energies, the trajectories being confined to N-dimensional tori in the phase space.[1] At higher energies the motion can become predominantly "stochastic" or "irregular," displaying great sensitivity to small changes in initial conditions and wandering over large portions of the energetically accessible phase space. (The term "stochastic" is used to imply a chaotic, randomlike behavior—the motion is still, of course, deterministic.) In a study of the quantum mechanical wave functions of a system with a (2:1) Fermi resonance we noted an analogous behavior. Namely, in the quasiperiodic regime, the wave functions tended to be localized in well-defined regions of configuration space. On the other hand, in the stochastic regime, the wave functions spread over most of the allowed configuration space.[2]

In the present paper we explore several aspects of the quantal energy spectrum: (a) the continuation of certain sequences of eigenvalues from the quasiperiodic to the chaotic regime, (b) the "second differences" $\Delta^2 E_i$ of the eigenvalues, i.e., their sensitivity to small changes in perturbation, (c) classical spectra in both regimes and a comparison with quantal spectra in the quasiperiodic regime, and (d) a comparison of "classical" and quantal number of states.

At low energies one expects to see regular sequencies of eigenvalues. At high energies it has been predicted[3] that the spectrum will, instead, be "irregular" and that the eigenvalues will be very sensitive to external perturbations. Evidence for this predicted behavior has been reported[4] in a study of a Henon–Heiles Hamiltonian[5] of the form

$$H=\tfrac{1}{2}(p_x^2+p_y^2+x^2+y^2)+\lambda(x^2y-\tfrac{1}{3}x^3)\,. \qquad (1.1)$$

We have made a detailed investigation of this system, but with a somewhat different value of λ (0.1118) from that used in Ref. 4 (0.088). Our results reported below, reveal a number of interesting features. These include (a) regular sequences of eigenvalues which continue smoothly from the quasiperiodic into the classically stochastic regime, a result which was initially quite unexpected, and (b) the presence of both "crossings" and "avoided crossings" of eigenvalues as small changes in the perturbation parameter λ are made. The former leads to spuriously large $\Delta^2 E_i$'s whereas the latter leads to genuinely large $\Delta^2 E_i$'s. Finally, it should be remarked that the Henon–Heiles system is somewhat atypical by virtue of its 1:1 degeneracy. However, it is this symmetry that enables us to identify more readily the course of various eigenvalues under perturbation and to see whether various sequences are present.

II. EIGENVALUES, SEQUENCES, AND SECOND DIFFERENCES

When converted to polar coordinates one sees that the energy eigenvalues for Hamiltonian (1.1) have A and E symmetry, i.e., nondegenerate and degenerate eigenvalues respectively.[6] Useful quantum numbers are n, the principal quantum number, and l, an approximate angular momentum quantum number (exact when $\lambda=0$[7]). The latter takes the values $l=0, \pm 2, \ldots, \pm n$ for even n and $l=\pm 1, \pm 3, \ldots, \pm n$ for odd n. The E states are those for which l is not a multiple of 3 or not equal to zero.[6] All $l\neq 0$ states are degenerate when $\lambda=0$.

The eigenvalues are given in Table I for all states for which $n\geq 9$. They were obtained from a variational cal-

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TABLE I. Energy eigenvalues E_q for the Henon–Heiles Hamiltonian.[a]

n	l	E_q	n	l	E_q
9	±1	9.444	11	±7	11.534
9	±3	9.467	11	±9	11.750
		9.552			11.752
9	±5	9.629	12	0	11.966
9	±7	9.794	12	±2	11.968
9	±9	10.035	11	±11	12.065
		10.036			
10	0	10.305	12	±4	12.206
10	±2	10.318	12	±6	12.277
					12.334
10	±4	10.463	12	±8	12.480
10	±6	10.573	12	±10	12.712
		10.590			
10	±8	10.774	12	±12	13.077
					13.087
10	±10	11.050	13	±1	12.762
11	±1	11.152	13	±3	12.748
					13.032
11	±3	11.160	13	±5	13.081
		11.325			
11	±5	11.383	13	±7	13.233

[a]Equation (1); $\lambda = (0.11180)$. The unperturbed energy equals $n+1$.

culation using a basis set of 990 functions. A test case was checked with a basis set of 1225 functions and no difference was found. The eigenvalues for $n \leq 8$, which will also be required here, are given in Ref. 6. Other studies of the system (1.1) have been made both quantally and semiclassically.[9] An initial assignment of quantum numbers was made on the basis that the ordering of levels is $E_{n+1} > E_n$, regardless of l, and $E_{n,l+2} > E_{n,l}$. An additional check is provided by the fact that for the doubly degenerate (E) states l cannot be a multiple of three. For all levels at or below (11, ±11) the above assignment placed the E states in their correct positions amid the A states. However, for some of the higher levels more care was required to make the assignments. As described below, irregularities in certain sequences of eigenvalues and anomalously large second differences indicated an incorrect assignment. Inspection of the eigenvectors themselves was used to distinguish the (11, ±11) E state from the (12, ±2) E state, the former having a large contribution from high angular momentum basis functions. The (12, ±10) and (13, ±1) states were similarly checked.

The regime of predominantly stochastic motion sets in at around $E = 9.0$, which is about 2/3 of the well depth of 13.33. Roughly one-half of all the 99 bound states are in this regime, i.e., between $E = 9.0$ and dissociation. Certain quasiperiodic regions are nevertheless also present here and we were able in fact to locate the eigentrajectories[6] for the states ($n = 9$, $l = \pm 9$), (10, ±10), and 11, ±11) and hence determine these eigenvalues semiclassically. Almost all the states with $n \leq 8$ have also been determined semiclassically.[8]

In Table II we show sequences of differences of quantal eigenvalues in both the quasiperiodic and stochastic regimes. The sequences are for (i) high l: $(n, \pm n) \rightarrow [n+1, \pm(n+1)]$, (ii) intermediate l: $[n, \pm(n-4)] \rightarrow (n+1, \pm(n-3)]$, and (iii) low l $(n, \pm 1) \rightarrow (n+1, 0)$ and $(n, 0) \rightarrow (n+1, \pm 1)$ for odd and even n respectively. Only in the sequence of high l states are all the states in regions of quasiperiodic classical motion. Nevertheless, for the other sequences, the entry into the stochastic regime ($n \geq 9$) has surprisingly little effect on their regularity (Table II). Indeed, an initially observed irregularity in the low l sequence was found to be due to an incorrect assignment of quantum numbers!

Second differences of eigenvalues were calculated from

$$\Delta^2 E_i = E_i(\lambda + \delta\lambda) - 2E_i(\lambda) + E_i(\lambda - \delta\lambda) \qquad (2.1)$$

using a $\delta\lambda = 0.001$. The $-\Delta^2 E_i$'s are divided by E_i for normalization. The results are those plotted in Fig. 1, and several others mentioned later. All values are positive other than the two not depicted in Fig. 1. Apart from two distinctly large values of $\Delta^2 E_i / E_i$, which we discuss below and which are not in Fig. 1, the second differences seem to form distinct families. (Specific values are given below.) The family of smaller $-\Delta^2 E_i / E_i$'s tended to belong to those states with high l quantum numbers whereas the family with the larger $-\Delta^2 E_i / E_i$'s belonged to states with low l. This behavior would appear to be consistent with the underlying classical dynamics. All the high l states are associated with stable (quasiperiodic) motion, even in the predominantly stochastic regime. On the other hand the low l states, when they could be computed semiclassically, that is at low n, were found to be associated with eigentrajectories near the regions that first became unstable (stochastic) at higher energies. (These regions are at values of l ranging from ±1 at low n to ±3 at the highest n.)

TABLE II. Differences of eigenvalues for various sequences.[a]

Transition			Transition		
$n\ l \rightarrow$	$n\ l$	ΔE	$n\ l \rightarrow$	$n\ l$	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

[a]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 uncertanties 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.

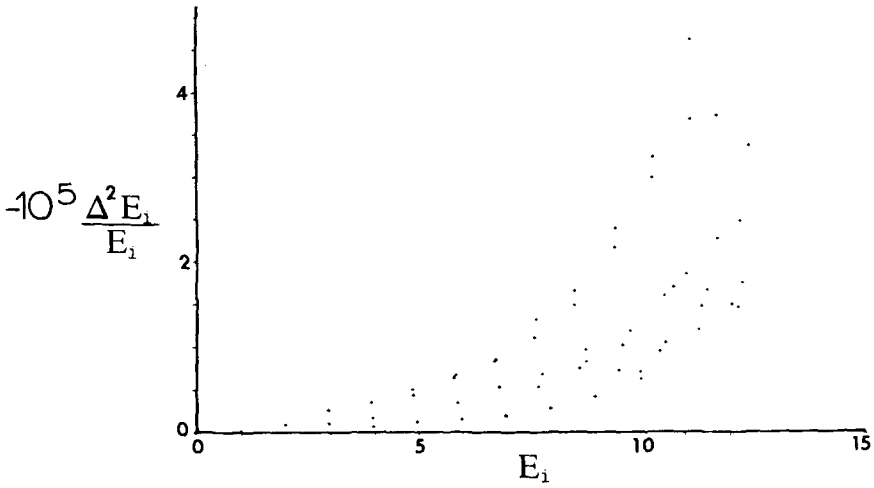

FIG. 1. The normalized second differences $-\Delta^2 E_i/E_i$ as a function of energy E_i. Omitted are several (off-the-graph) values listed in the text.

For example, for the states $(n, \pm n)$ the values of $-\Delta^2 E_i/E_i$ for $n=1, 3, 5, 7, 9, 11$ are $(\times 10^{-5})$ 0.088, 0.165, and 0.0649, 0.156, 0.285, 0.705, and 0.621, 1.48, respectively. Similarly low values are obtained for even n's in this $(n, \pm n)$ series. As an example of another series, $(n, \pm 1)$, the values of $-\Delta^2 E_i/E_i$ for $n=1, 3, 5, 7, 9$, and 11 are $(\times 10^{-5})$ 0.088, 0.350, 0.642, 1.11, 2.15, 3.66, respectively, and so are typically larger than those for the $(n, \pm n)$ family. Not shown in Fig. 1 are several large (off-the-graph) values (5.63, 7.43 and 11.2×10^{-5}) associated with the (12, 0) (12, ±2), and (13, ±3) states, respectively, all of which are for states lying near classical separatrices. Also not shown are the values for the (13, ±1) and (12, ±10) states, which are discussed below, -34.7 and 48.6×10^{-5}, respectively.

These two largest values of $-\Delta^2 E_i/E_i$, -34.7, and 48.6×10^{-5}, can be understood when we plot (Fig. 2) the eigenvalues as a function of λ. For the states (13, ±1) and (12, ±10) there appears to be an "avoided crossing." This behavior is further evidenced by the fact that the $-\Delta^2 E_i/E_i$ associated with the (13, ±1) E states is negative whereas that for the (12, ±10) E states is positive. Of all the 99 bound states only the (13, ±1) states had genuinely negative $-\Delta^2 E_i/E_i$'s. Four other (apparently) large values of $-\Delta^2 E_i/E_i$ were also observed initially (74.4, -94.1, 100.3, -77.3×10^{-5}) but closer inspection showed these four to be spurious, namely to be due to the (13, ±5) E states *crossing* the (12, ±12) states (which are split because l is a multiple of three). The level crossing, which is permitted because the (13, ±5) and (12, ±12) states are of different symmetry, is also shown in Fig. 2. The significance of the true avoided crossing will be discussed later.

Parenthetically, we note that in the vicinity of an isolated avoided crossing of two eigenvalues one can approximate the behavior, if one wished, by a two-state Hamiltonian with diabatic basis elements $\bar{H}_{ij}(\lambda)$, $i, j = 1, 2$, chosen so that the corresponding two adiabatic curves $E_n(\lambda)$, equal to $\frac{1}{2}\{(H_{11}+H_{22}) \pm [(H_{11}-H_{22})^2+4H_{12}^2]^{1/2}\}$, would approximately fit the two exact ones in this λ neighborhood. If one then lets $\bar{H}_{12}\to 0$, these curves would cross, instead of avoiding each other. In the exact Hamiltonian, on the other hand, which generates all the curves $E_n(\lambda)$ there is no parameter such as $\bar{H}_{12}(\lambda)$ which, upon vanishing, makes the curves cross at that λ.

We have illustrated in Fig. 2 an avoided crossing in one region of λ. Further avoided crossings may also occur in other λ neighborhoods. Incidentally, the word "crossing" is used throughout in the (conventional) sense of two energy levels crossing each other when they are plotted as a function of some parameter (λ).

III. CLASSICAL AND QUANTAL POWER SPECTRA

In the quasiperiodic regime we are able to make a direct comparison between the classical power spectrum,

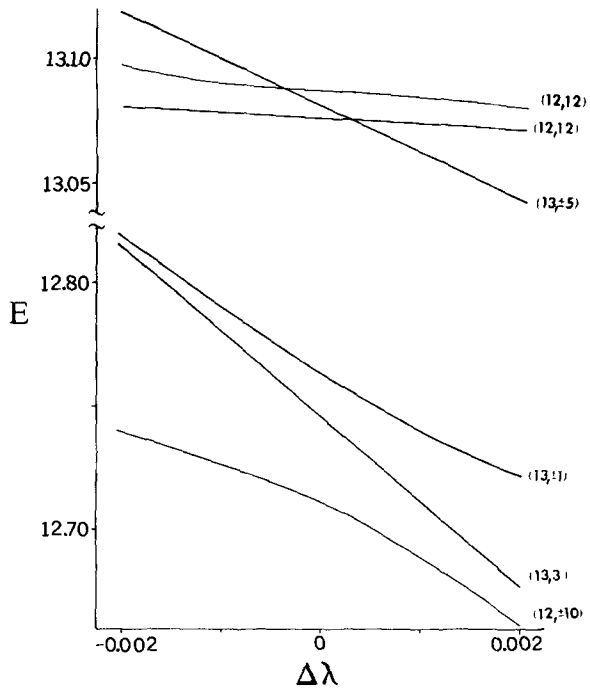

FIG. 2. Plot of the eigenvalue E_i as a function of the perturbation parameters λ. The diagram shows the repulstion of levels between the (13, ±1) and (12, ±10) states and the level crossing of the (13, ±5) and (12, ±12) states. The (12, ±12) degeneracy has been removed, and we have labeled these two states simply by (12, 12).

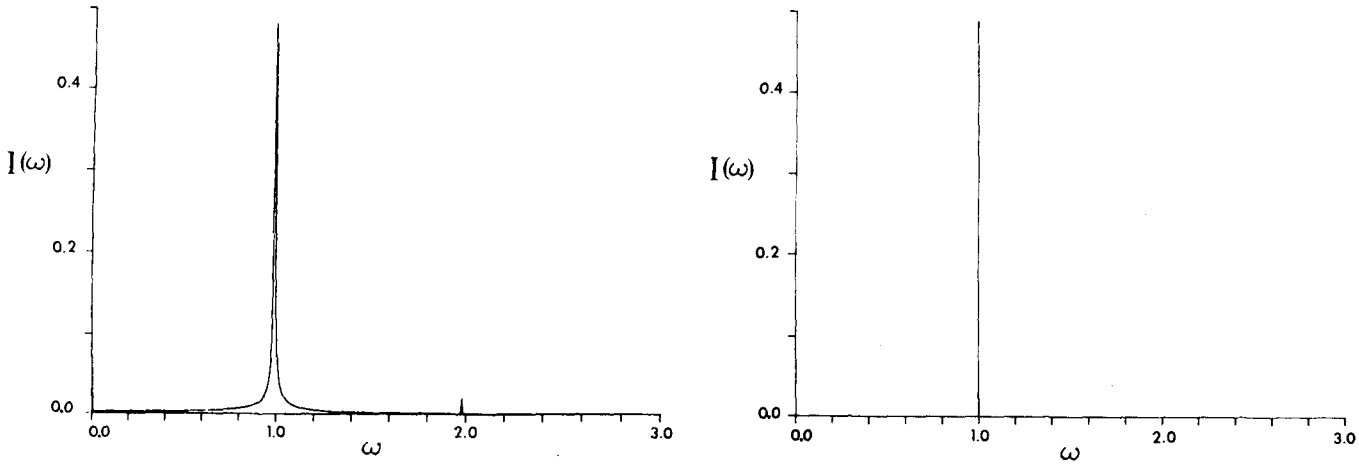

FIG. 3. (a) Classical power spectrum, $I(\omega)$ of the x coordinate for the ground state; the peak height is 0.48. $E = 0.9986$. The eigentrajectory corresponding semiclassically[6] to the quantum ground state is used; (b) Quantum spectrum corresponding to a. The peak height is 0.49. $E = 0.9986$. (300 basis elements were used.)

calculated from the Fourier transform of classical trajectories, and the spectrum of quantal transitions: Since we are looking at transitions between pure states (the molecules are assumed isolated), one may show explicitly how, in the limit $h \to 0$, the quantal and classical power spectra become identical. This is demonstrated in Appendix I. In Fig. 3 we compare classical and quantal spectra in the quasiperiodic regime at $E = 0.9986$. The details of how such computations are made has been described elsewhere.[10–12] It should be noted that (for quasiperiodic motion) the broadening of the lines in the classical spectrum is entirely an artifact of the finite length (in time) of the classical trajectory that is Fourier analyzed. Our results show good agreement between the quantal and classical spectra both in the positions of the lines and their intensities; the latter corresponding to the transition probabilities.

Although the "correspondence" between quantal and classical spectra in the quasiperiodic regime is well understood[13] no such clear picture emerges in the stochastic regime.[3] Here the classical trajectories display power spectra of great complexity. In Fig. 4 we show the power spectra of two stochastic trajectories at the same energy but with different initial conditions. One trajectory corresponds to motion that is, in the sense of the zero order Hamiltonian [i.e., $\lambda = 0$ in Eq. (1.1)], of high angular momentum and the other of low angular momentum. The fact that the two spectra are different indicates that the phase space of the system, at the energy considered, is strongly divided, i.e., the trajectories are not ergodic over the whole of the energy shell. Furthermore, it is not clear that in the stochastic regime there will be a correspondence between the spectrum of an individual trajectory and the quantal spectrum. In the quasiperiodic regime the classical spectrum is that of a trajectory which, in the semiclassical limit, belongs to the phase space manifold (the torus) with which the corresponding quantal state can be associated. It may well be that in the stochastic regime the quantal states will be associated, in the limit $h \to 0$, with the whole energy shell. In this case the classical

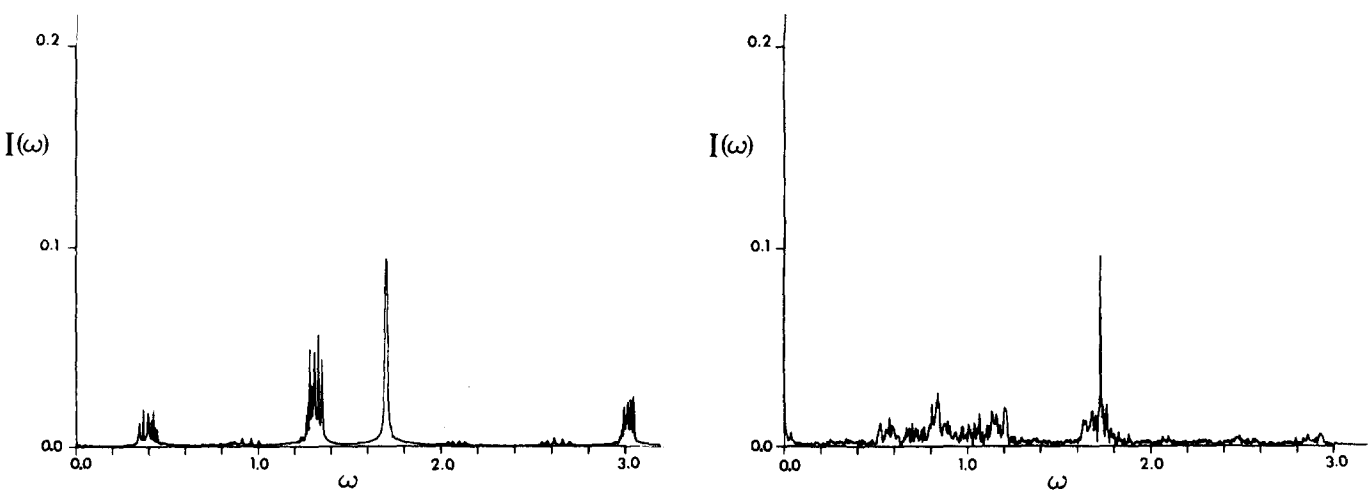

FIG. 4. (a) Classical power spectrum of high angular momentum trajectory at $E = 11.16$; (b) Classical power spectrum of low angular momentum trajectory at $E = 11.16$.

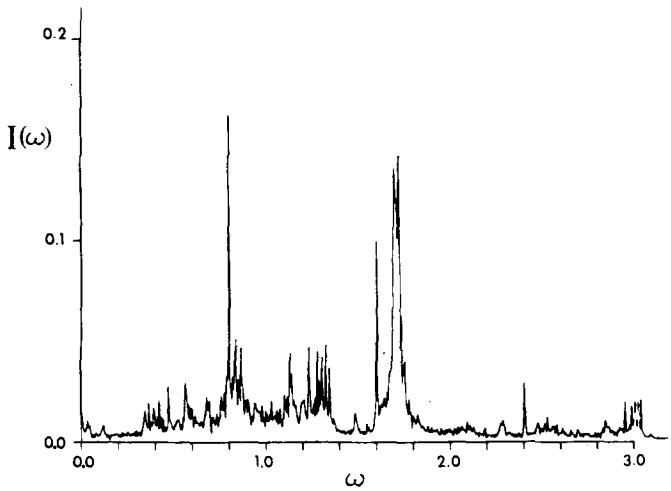

FIG. 5. Classical power spectrum microcanonically averaged at $E = 11.16$.

spectrum should be obtained from the dipole correlation function computed over the microcanonical ensemble. (The behavior of correlation functions in the quasiperiodic and stochastic regimes is described elsewhere).[14] In Fig. 5 we show the microcanonically averaged power spectrum. In order to compare this spectrum with the quantal spectrum it may be necessary to take the latter as an average over some family of states, and we plan to explore this topic in a later paper.

IV. "CLASSICAL" AND QUANTAL NUMBER OF STATES

In studies of unimolecular reaction rate theory,[15] particularly for comparison with classical trajectory results, it is useful to have a method of calculating the number and density of states for nonseparable systems. The "classical" number of states with an energy $\leq E$, $N_{cl}(E)$, for a system of n degrees of freedom is simply given by

$$N_{cl}(E) = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p} \int d\mathbf{q}\, \theta[E - H(\mathbf{p}, \mathbf{q})] , \qquad (4.1)$$

where p and q are the n dimensional vectors of momentum and conjugate coordinate respectively. θ is the (unit) step function. (The density of states is just $dN_{cl}(E)/dE$. This is expressed by replacing the step function in (4.1) by a delta function.) The integral (4.1) can be evaluated quite rapidly using efficient Monte Carlo procedures. In Figs. 6 and 7 we compare the smooth $N_{cl}(E)$ with the corresponding exact quantal result. The agreement is very good and in fact at high energies the simple "quantization condition" $N_{cl}(E)$ = integer can give quite good agreement with the exact quantal eigenvalues.[15] At these high energies the agreement is not better than the mean separation; clearly any more sophisticated quantization procedure must do better than this. Finally, by analogy with known results[16] in the separable case, a large deviation between classical and quantal results at moderate energies is anticipated when a system of higher number of degrees of freedom is considered. At higher energies, though, the deviation will become minor.

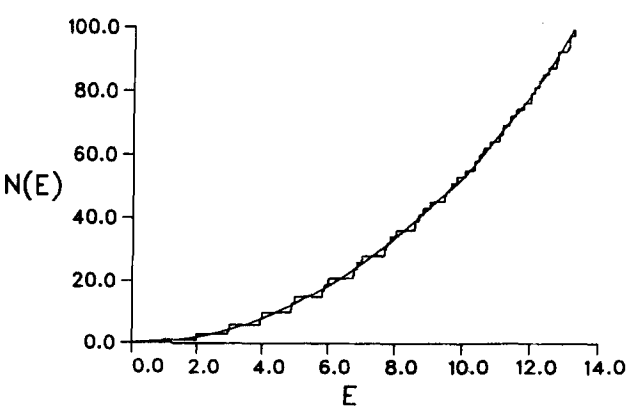

FIG. 6. Comparison of the "classical" and quantal number of states. For the classical number N denotes the N_{cl} given by Eq. (4.1).

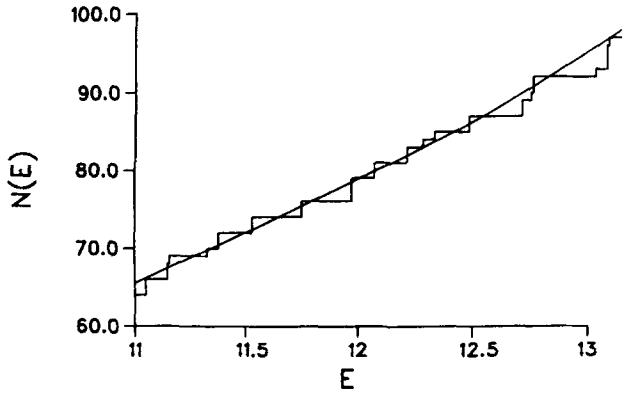

FIG. 7. An enlargement of Fig. 6 in the high energy region.

V. CONCLUSIONS AND REMARKS ON "QUANTUM STOCHASTICITY"

We believe that the presence of both "crossings" and "avoided crossings" is of particular importance. If the former is not taken into account spuriously large second differences will be obtained. The latter is responsible for genuinely large second differences. For our system ($\lambda = 0.1118$) we only observe two large $\Delta^2 E_i/E_i$'s corresponding to the one "avoided crossing" between the (13, ±1) and (12, ±10) E states. This is to be compared with the investigation of Pomphrey[4] where many more large $\Delta^2 E_i$'s are observed. In this case ($\lambda = 0.088$) the system supports more bound states, i.e., the system is nearer the semiclassical ($\hbar \to 0$) limit. Since Pomphrey's calculations involve states of only one symmetry species we conclude that his large $\Delta^2 E_i$'s are due to the presence of many "avoided crossings."

The presence of avoided crossings may have a deeper significance. The avoided crossings are in λ space, and an "avoided crossing" corresponds to the presence of a "resonance." If each state is simultaneously involved in numerous avoided crossings the relevant eigenvectors will adopt a rather statistical character. This notion,[17] which in the semiclassical limit is analogous to Chirikov's theory of overlapping resonances,[18] may pro-

vide a criterion for the onset of "quantum stochasticity." Further tests of this conjecture are now in progress.

The relationship between the classical and quantum power spectra and their behavior in the stochastic regime is of importance to IR multiphoton dissociation. The time dependent classical and quantum spectra have been calculated for a model of a triatomic molecule in a laser field. Initially, the spectra consist of a very few lines but a transition to a stochastic type spectrum consisting of many lines occurs both quantally and classically.[19]

Recent interesting results on nodal lines and natural orbitals have been obtained,[20] and it would be useful to make plots such as the present Fig. 2 to see if there is an avoided crossing and whether it is an isolated one or an overlapping one. Only in the second instance, we would contend, might the wave function take on a statistical character.

The present description of "quantum stochasticity" as being associated with overlapping avoided crossings in eigenvalue vs parameter plots differs from a description given elsewhere.[8] The latter criterion involved[8] projecting the wave function onto those at $\lambda = 0$ and so was basis set dependent.[8,21] The conclusions regarding the quantum stochasticity of the Henon–Heiles system for the parameter chosen are quite different from those described in this paper. Other aspects of quantum stochasticity have been discussed (e.g., Ref. 22) and have been discussed in a recent review,[23] which also reviews developments in classical stochasticity.

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APPENDIX I

Here we examine the relationship between quantal spectra and the classical spectrum of quasiperiodic motion.

In the Heisenberg representation the quantal correlation function is

$$C(t) = \sum_n \rho_{nn} \langle n | \hat{\mu}(0)\hat{\mu}(t) | n \rangle , \tag{A1}$$

where the ρ_{nn} are the diagonal elements of the density matrix and $\hat{\mu}$ the dipole operator. Using the standard result

$$\hat{\mu}(t) = e^{i\hat{H}t/\hbar}\hat{\mu}(0)e^{-i\hat{H}t/\hbar} , \tag{A2}$$

and assuming the states $|n\rangle$ to be the exact eigenstates of $\hat{H}$ (we are considering the spectrum of an isolated molecule) (A1) is converted to the Schrödinger form

$$C(t) = \sum_n \rho_{nn} \sum_k |\langle k | \hat{\mu}(0) | n \rangle|^2 e^{i(E_k - E_n)t/\hbar} . \tag{A3}$$

The power spectrum is just

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) e^{i\omega t} dt , \tag{A4}$$

yielding

$$I(\omega) = \sum_k |\langle k | \hat{\mu}(0) | n \rangle|^2 \delta \left(\omega - \frac{(E_n - E_k)}{\hbar} \right) , \tag{A5}$$

where for simplicity we have assumed that only the nth state is populated (i.e., $\rho_{nn} = 1$).

We now consider the matrix element

$$\mu_{kn} = \langle k | \hat{\mu}(0) | n \rangle . \tag{A6}$$

For quasiperiodic classical motion the states $|n\rangle$ can be approximated by their action-angle representation, i.e.,

$$|n\rangle = e^{2\pi i n w} \tag{A7}$$

(here we work, without loss of generality, with one-dimensional motion). Since the motion is assumed quasiperiodic the dipole moment can be expressed as a Fourier series, classically as,

$$\mu = \mu(I, w) = \sum_s \mu_s(I) e^{2\pi i s w} , \tag{A8}$$

where $\mu_s(I)$ are a set of Fourier coefficients which are functions only of the classical action variable I; w is the conjugate angle variable. The dipole operator can be expressed as

$$\mu = \sum |k\rangle \langle k | \mu | n \rangle \langle n | \equiv \sum_{k,n} \mu_{kn} |k\rangle \langle n| . \tag{A9}$$

Using (A7) to (A9) the matrix elements μ_{kn} are easily related to μ_s,

$$\mu_{kn} = \sum_s \mu_s(nh) \delta_{k-n,s} , \tag{A10}$$

and hence the power spectrum becomes

$$I(\omega) = \sum_k \sum_s |\mu_s(nh)\delta_{k-n,s}|^2 \delta \left(\omega - \frac{(E_n - E_k)}{\hbar} \right) . \tag{A11}$$

The last stage is as follows. The eigenvalues E_n and E_k are approximated by their EBK values, i.e., apart from the $\frac{1}{2}h$ terms considered later,

$$E_n = H(I = nh); \; E_k = H(I = kh) , \tag{A12}$$

where the Hamiltonian, since it is integrable, is expressed in terms of the action variable. Hence to first order we have

$$E_n - E_k \simeq (k - n)h \left(\frac{\delta H}{\delta I} \right)_{I = nh} \equiv (k - n)\hbar \, \omega(nh) , \tag{A13}$$

where $\omega(nh)$ is the classical angular frequency associated with the torus with action $I = nh$. Substituting (A13) into (A11) and using the Kronecker delta $\delta_{k-n,s}$ gives the final result.

$$I(\omega) = \sum_s |\mu_s(nh)|^2 \delta[\omega - s\omega(nh)] . \tag{A14}$$

This is exactly the classical power spectrum of motion on the torus of action $I = nh$.[3] For brevity, we omitted the usual $\frac{1}{2}h$ terms in the energy eigenvalues of the os-

cillators. They cancel in the final result, but the $\mu_s(nh)$ and $\omega(nh)$ are replaced by $\mu_s(nh+\frac{1}{2}h)$ and $\omega(nh+\frac{1}{2}h)$.

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