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CHAOTIC MOTIONS IN VIBRATING MOLECULES: THE GENERALIZED HÉNON–HEILES MODEL

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The method of avoided crossings is applied to a simple molecular model, the generalized Henon–Heiles system of coupled oscillators. The aim here is to determine the onset of wide-spread chaotic motions. The method is used to locate, in a simple manner, the resonances that lead to chaotic motions for different choices of parameters wherein the frequencies of the unperturbed oscillators are in the ratio 3 : 4 and 7 : 13. The accuracy of the prediction is verified against numerical calculations of classical trajectories.

1. Introduction

In recent years there has been considerable interest in the study of classically non-integrable dynamical systems. This has relevance to a variety of areas of research in physics and chemistry [1–3]; in particular the intramolecular dynamics of vibrationally excited molecules is often cast in the form of a problem in classical, non-linear dynamics. A major concern has been understanding the nature of intramolecular energy transfer in classical models of molecules. Here it is important to characterize the different kinds of motion that can occur [4–6]: regular or quasi-periodic, and irregular or chaotic. For an N-degree-of-freedom integrable, conservative system, the motion is confined to N-dimensional tori in the phase space [4]. Upon addition of a non-integrable perturbation chaotic motions can occur as well; the extent, or measure, of this latter type of motion is related to the relative size of the perturbation. The KAM theorem [4–6] which deals with this general problem, and numerous applications have been extensively reviewed recently [7–9].

This paper is concerned with the behaviour of "molecular" systems with $N = 2$ degrees of freedom. The main objective here is in the nature of an ab initio prediction of when the character of the overall motion changes from being largely regular to a mixture of regular and chaotic motions — the so-called chaotic transition. The hamiltonian studied here has two parameters, and is a generalization of the Hénon–Heiles system [10].

$$H = \tfrac{1}{2}(p_1^2 + p_2^2 + \omega_1^2 q_1^2 + \omega_2^2 q_2^2) - \epsilon q_1 q_2^2 - \lambda q_1^3 . \quad (1)$$

where the p_i and q_i refer to the momenta and coordinates of the two degrees of freedom, $i = 1, 2$, and the ω_i are the respective frequencies of the oscillators. The perturbation parameters are ϵ and λ.

A technique of detecting (by inference) the existence of chaotic motions has been proposed recently [11] for such coupled oscillator systems. This "method of avoided crossings", which is based on classical perturbation theory, has previously been successfully applied to two-degree-of-freedom systems with a single perturbation term; here it is applied to the hamiltonian (1).

Model systems, such as the one above have found much application in chemistry [3], being simple, prototypical molecules (with $N = 2$, this is the collinear triatom). By varying the parameters ω_i, ϵ and λ, one can mimic different molecular situations. In particular, this system has been quantized by a variety of semiclassical methods [12,13], to examine alternate, more tractable means of studying the quantum mechanics of molecules. When the classical motion is regular, well-known correspondence principles relate features of the classical motion to those of quantum-mechanical stationary states — this forms the so-called regular spectrum [14]. The absence of such a principle for classically irregular motions and quantum states

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has resulted in the semiclassical limit of such levels, the irregular spectrum [14], being rather less well understood. In addition, the study of classically chaotic motions has pertinence to intramolecular energy randomization [3,15]. It is generally believed that statistical theories apply when the classically irregular motions predominate.

In studies in non-linear dynamics, different criteria have been used [10,16,17] to determine whether the motion is regular or chaotic, and several methods [3, 18] have been proposed to predict the onset of chaotic motions. It is perhaps worth observing that in non-integrable systems, irregular regions exist at all energies, and most criteria for judging the nature of the motion depend on the extent of chaos. When the irregular regions are extremely narrow, these will not be readily apparent in numerical calculations that examine, say, the Poincaré surface of section [10] or the rate of separation of nearby trajectories [16] Thus the notion of a chaotic transition is poorly defined when dissociated from a sense of the extent of irregular behaviour. In this paper, we confine our interest to when this measure is sufficiently large ‡ to be detected by any simple criterion

The vibrational hamiltonians of systems of chemical interest are typically extensions of eq. (1). Thus it is necessary to explore more fully ab initio methods of predicting chaos in such systems. This paper is a step in that direction The method of avoided crossings, which is discussed in section 2, being far from a "black-box" technique, as such calls for judicious application. The instances where care must be taken, and additional caveats are also discussed in section 2. Section 3 deals with the predictions of the method, and the verification of the existence and onset of chaotic motions for choices of various parameters A discussion and summary follows in section 4

2. Theory

The hamiltonian considered here is given by eq. (1) and has as the unperturbed part,

$$H_0 = \tfrac{1}{2}(p_1^2 + \omega_1^2 q_1^2) + \tfrac{1}{2}(p_2^2 + \omega_2^2 q_2^2) . \qquad (2)$$

This is integrable, and action–angle variables [5] can be defined:

$$I_i = (\pi/\omega_i)(p_i^2 + \omega_i^2 q_i^2) .$$

$$\theta_i = \tan^{-1}(-p_i/\omega_i q_i) , \quad i = 1, 2 . \qquad (3)$$

Thus

$$H_0(\boldsymbol{p}, \boldsymbol{q}) \to H_0(\boldsymbol{I}) = (2\pi)^{-1}(I_1\omega_1 + I_2\omega_2) . \qquad (4)$$

Consequently, the motion of H_0 occurs on a 2-torus when ω_1/ω_2 is an irrational fraction, and consists of periodic orbits when this ratio is rational. The perturbation terms are

$$H_1 = -\epsilon q_1 q_2^2 , \quad H_2 = -\lambda q_1^3 .$$

The hamiltonian $H' = H_0 + H_1$ is the generalized Barbanis (GB) system [19], and $H = H_0 + H_1 + H_2$ is the generalized Hénon–Heiles (GHH) system. For a a small number of special values of the ratios ω_1/ω_2 and ϵ/λ, the system is actually integrable [20]; in the general case, however, no global canonical transformation exists which allows for an expression of H as a function of action variables alone. Specifically, for any non-zero ϵ, H' is always non-integrable. In this situation, the KAM theorem applies: for sufficiently small perturbations, most of the tori will still be preserved although in distorted form. Such systems have been termed quasi-integrable. Non-toroidal, i.e. chaotic motion is also possible, and the objective is to determine when such motions have appreciable measure. This is accomplished by the following procedure.

The method of avoided crossings [11]. Although this method has been presented earlier, it is worthwhile to recall the salient features.

(i) The hamiltonian $H(\boldsymbol{p}, \boldsymbol{q}; \epsilon, \lambda)$ is transformed to a Birkhoff normal form in new canonical variables $\boldsymbol{\xi}, \boldsymbol{\eta}$: $F(\boldsymbol{\xi}, \boldsymbol{\eta}, \epsilon, \lambda)$. F is an integrable approximation to some low order in the perturbation parameters, ϵ, λ. A further canonical transformation of this normal form to action–angle variables $\boldsymbol{I}, \boldsymbol{\theta}$, yields an approximation to H in terms of action variables alone, $F(\boldsymbol{\xi}, \boldsymbol{\eta}; \epsilon, \lambda) \to K(\boldsymbol{I}; \epsilon, \lambda)$. Since K and F are integrable hamiltonians, fixing a set of actions $\boldsymbol{I}$ defines a torus in the motion of F. Viewing H as arising from a non-integrable perturbation of F, by the KAM theory, some of these tori

‡ The practical considerations involved here usually make it difficult to observe chaotic motions by the Poincaré surface of section or by other methods if the measure of the irregular regions is less than 0.05–0.1. Hence the term "sufficiently large" as used in this paper will denote this approximate range.

will persist, and some will be destroyed. The former are denoted stable tori, and thus what is needed is a way to decide which tori will survive.

The stability criterion for tori is constructed by analogy with the quantum-mechanical case. With a single parameter, the generic behaviour of a quantum system is the absence of eigenvalue degeneracy [5]. Thus, in a graph of eigenvalue versus parameter variation, one observes an "avoided" crossing The use of non-degenerate perturbation theory [21], on the other hand, gives rise to crossing at approximately the same values (of energy and parameter) when an avoided crossing occurs in the full system. Thus a crossing in the perturbation approximation to the system is viewed as the signature of an avoided crossing in the eigenvalue spectrum of the actual system. (Exceptions to this are discussed in detail at the end of this section.)

Several avoided crossings within a small range (of energy, parameter) were interpreted [22] as giving rise to a quantum chaotic state. In the neighbourhood of a crossing, off-diagonal coupling extensively mixes the wavefunctions, so that if enough states are involved in a crossing, i.e. a *multiple* avoided crossing, the expectation value of a given dynamical quantity in the quantum chaotic state might approximate the classical microcanonical average at that energy.

By the standard quantum–semiclassical correspondence principle [14], an invariant torus is identified as the analogue of a stationary wavefunction Therefore, the semiclassical interpretation of the mixing that occurs at a multiple avoided crossing is essentially a statement of toroidal instability for the tori involved [‡]. The invariant tori that correspond to quantum stationary states are those that can be quantized by the EBKM rules [14,24], those for which

$$\oint_{C_i} \boldsymbol{p}\cdot \mathrm{d}\boldsymbol{q} = (n_i + \alpha_i/4)h \ , \quad i = 1, 2 \ . \tag{5}$$

Here C_i denotes a topologically distinct path, α_i is the Maslov index, h Planck's constant and the n_i are integers.

[‡] It is as if an orbit which is originally confined to the portion of the energy shell occupied by one torus, is able to wander in the regions occupied by other tori, and this "superposition" of different motions gives an apparently random behaviour See e g fig 9 in ref [23].

(ii) This criterion for torus instability is extended to all tori by invoking a lattice structure in the space of actions (with some chosen unit of action), thereby selecting for further examination, sets of actions with integer separation. The classical eigenvalues for this set of actions are examined as a function of the perturbation parameter(s). The term eigenvalue is used in analogy with semiclassical mechanics, and the set of actions as chosen here is arbitrary, save for the lattice structure.

$$\{n + \alpha/4 + \chi \,|\, -\alpha/4 \leqslant \chi \leqslant \alpha/4, n \in Z^N\} \ .$$

By varying χ, one searches for the occurrence of multiple crossings in a small neighbourhood of parameter values, around the particular value of interest. The unit of action is chosen (see below) to be small enough to detect the effect of the perturbation. From this examination, one may determine the onset of chaotic motions as the lowest energy at which multiple (and overlapping) avoided crossings occur. Usually this happens for $\chi = -\alpha/4$.

In purely classical terms, the above method is merely a graphic procedure for determining resonant periodic orbits and their multiple overlaps [3,11,25]. The imposed lattice structure, as a grid of actions, ensures that at every avoided crossing, there is a zero-frequency and hence a resonant periodic orbit, and by using the appropriate scale for the unit of action, the overlapping of these resonances is taken into account

In an earlier publication [11], this method was applied to the cases of cubic and quartic non-linearities in coupled oscillator systems with a single perturbation term. For the GHH hamiltonian, the classical perturbation method of the Lie transform [26] is applied to obtain the F and K polynomials [see (i)], these are given in the appendix.

A point that needs to be discussed here is the role of the unit of action in relation to the perturbation parameters ϵ and λ. The present approach is a semiclassical one, in the sense that classical and quantal conceptual methods are mixed. We have remarked earlier that in addition to locating avoided crossings, one must also estimate their width to determine the extent of overlap — it is the multiple overlapping of avoided crossings that leads to chaos [11].

In a discussion of the quantal irregular spectrum, Berry [27] has distinguished, for fixed perturbation parameter values (ϵ,λ), three semiclassical limits de-

pending on the relative size of Planck's constant h. When h is relatively large (regime 1), the volume of phase space associated with a quantum state can be larger than the chaotic regions. Hence almost every semiclassical state would be insensitive to the underlying dynamics – almost any perturbation theory would work. In terms of the present analysis, few states would be involved in avoided crossings. If h is very small (regime 3), then the volume of phase space associated with each quantum state would be proportionately smaller, and almost every quantum state would be sensitive to the classical dynamics. Thus, there would be several avoided crossings, but neither would the degree of avoidance be large, or would the overlap between the crossings be significant. For intermediate h (regime 2), both regular and irregular quantum states coexist. In this regime, the unit of action is neither so large as to have too few avoided crossings, nor so small as to have too many, but insignificant avoided crossings.

As the interest here is in being able to estimate the gross features of the classical motion, when the measure of the chaotic flows becomes appreciable, it is regime 2 that is of interest. The unit of action is to be chosen so that the relative volume associated with a given state will be sensitive to an appreciable amount of chaotic motion. From earlier studies of some systems, there is an indication of the relative size of h that is appropriate. For the GHH with $\omega_1 = \omega_2 = 1$, $\lambda = -\epsilon/3$, $\epsilon = -(80)^{-1/2}$ and $h/2\pi = 1$, it was found that avoided crossings were sparse [21,28]. The system, which dissociates at an energy of 13.33 supported only 100 bound levels (the effective number is even lower because symmetry separates these into non-interacting sets of ≈65 and 35 states). This corresponds to the semiclassical regime 1; with $\hbar = 0.62$ (or equivalently, with $\epsilon = -0.088$), the system has twice the number of bound states, and there are several avoided crossings [21], indicating that for this value of h, ϵ is consistent with regime 2 discussed above. In the examples studied in this paper, the parameters ϵ, λ and the unit of action have been adjusted such that the average density of states conforms more closely with the latter system.

At this stage it is appropriate to identify some of the shortcomings of the method. First, this technique is based on a perturbation scheme, and it can be relied upon only if all parameters are of the appropriate relative size. This is usually true in molecular systems, when a normal-mode picture is a good starting point. Secondly, and more importantly, there are several examples of systems wherein both real crossings (actual degeneracy) and avoided crossings can occur in the quantum-mechanical spectrum as a parameter is varied [‡], while the classical motion is regular. On the basis of perturbation theory alone, it is impossible to distinguish between the avoided crossings of integrable and non-integrable systems; thus the inferences drawn above [see (i)] can be quite erroneous. It seems simplest at this stage to *exclude* integrable systems from such analysis. Recent developments [30] have made it possible to determine whether a system is integrable by using the Painlevé property. When applied to the GHH, this indicates that the system is integrable for the cases [20] $\lambda/\epsilon = 2$ and $(\omega_1/\omega_2, \lambda/\epsilon) = (1, 1/3)$ and $(4, 16/3)$. The method of avoided crossings cannot be applied in these instances. In addition, the pseudo-integrable case [29] (where the motion is regular, but not on a torus) should be excluded as well, although for systems such as (1) with smooth potentials, this exceptional behaviour is unlikely to occur. The requirement of an external check to exclude certain types of systems is a deficiency of the method, it awaits further research to device correspondingly satisfactory internal checks.

3. Applications

The GHH system is best treated as a further perturbed GB system; one reason being that the term H_2 is not capable of introducing any real degeneracies in the eigenvalue spectrum. Thus any avoided crossings in H' will remain avoided crossings in H. By using the expressions for the canonical transformations given in the appendix, the energy versus parameter curves can be obtained in a straightforward manner. We first consider H_0 as the basic hamiltonian out of which the GB arises; thus ϵ is varied around the value of interest with $\lambda = 0$. This gives information regarding the

[‡] See, e.g. ref. [29]. The system studied here, a billiard whose boundary is a polygon with angles a rational multiple of π is somewhat special: there exist n independent constants of the motion, which occurs on a multiply handed sphere, *not* a torus. Richens and Berry have termed this type of regular behaviour pseudo-integrability.

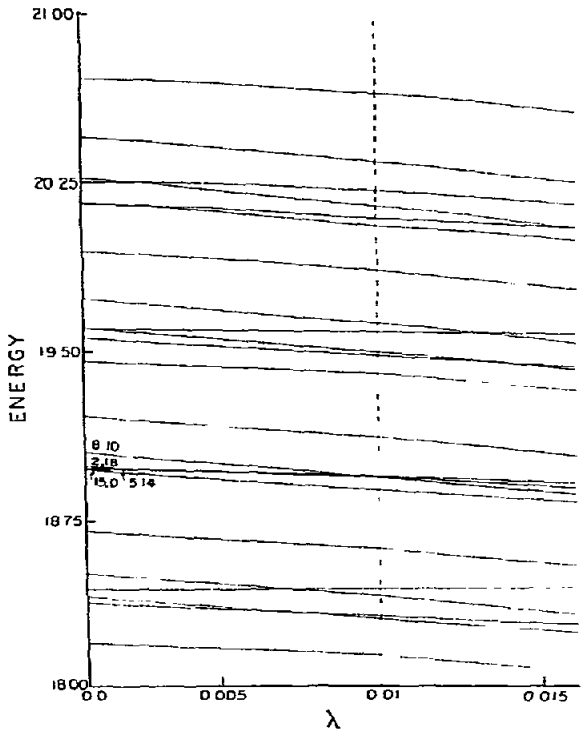

Fig. 1 Constant-action curves for the GHH system with $\omega_1^2 = 1.6$, $\omega_2^2 = 0.9$, and $\epsilon = 0.08$, $\chi = -1/2$, $c = 1$, as a function of the perturbation parameter λ. The curves are indexed by integers (n_1, n_2) [see eq (A 3)]

avoided crossings in the GB system. (Note that there can be no real crossings in any GB system.) The further avoided crossings induced by then varying λ yields the required information in the corresponding GHH system. This analysis is performed for two different choices of the parameters.

In the first, the frequencies and perturbation parameters are: $\omega_1^2 = 1.6$, $\omega_2^2 = 0.9$, $\epsilon = 0.08$, $\lambda = 0.01$. There have been some previous studies [11,31] of the system with $\lambda = 0$. Trajectory calculations by Sorbie and Handy [31] gave evidence for the existence of appreciable chaotic motions at an energy of ≈ 19 units, and the system dissociates at 25.3125 units. The present method, when applied to this GB system showed a lowest set of avoided crossings at around the same energy [11].

The eigenvalue curves [‡] under further variation of λ (with fixed $\epsilon = 0.08$) are shown in fig. 1. The system dissociates at 23.53 units for $\lambda = 0.01$, the lowest avoided crossings again occur at around 18.9 units. Varying c by a small amount between $c = 0.9$ and $c = 1$, does not change this lowest energy of multiple avoided crossings substantially; further, the same set of action curves [‡] is involved in the avoided crossings in both the GB and the corresponding GHH system. The direct implications are that (1) in the GHH system, the onset of widespread chaos occurs at an energy only marginally lower than in the corresponding GB system, and (2) in both systems, the route towards large-scale chaos is very similar and this chaos occurs in the same kind of region of phase space in either system.

These predictions can be checked by computing trajectories for the latter system. A simple visual criterion for determining whether the motion is regular or not is the Poincaré surface of section. Using several trajectories on the energy shell, one can examine the overall structure of the phase space. Below E (the total energy) = 18 units, it is difficult to locate any chaotic orbits, for the reasons outlined in section 1. Most tori are preserved as in the KAM theory. At $E = 19$ units, on the other hand, the fraction of chaotic trajectories is measurable which indicates that the chaotic transition does indeed occur around this energy. The surfaces of section at the two energies are shown in fig. 2. One can see that the chaotic regions in fig. 2b are indeed analogous to the regions of phase space that first show widespread irregular behaviour in the GB system with $\lambda = 0$ (see fig. 3 in ref. [31]).

The second system treated here has parameters: $\omega_1^2 = 0.49$, $\omega_2^2 = 1.69$, $\epsilon = 0.1$, $\lambda = 0.01$. The lowest few eigenvalues for this system have been obtained from trajectory [12] and perturbation [13] methods. The interest in these particular parameter values is due to observations by Hutchinson and Wyatt [32] that the Wigner function [27] for the quantum states in this system shows regular quantal behaviour for all bound states, and unlike most systems that have been studied, classical chaotic motions occur only at very high energies relative to dissociation, and even here, a substantial fraction of the tori still survives. It may

[‡] The symmetry of the perturbation term H_1 separates the bound states into two mutually non-interacting sets, $\{n_1, n_2 | n_2 = 1, 3, 5, \ldots$, odd integers$\}$ and $\{n_1, n_2 | n_2 = 0, 2, 4, \ldots$, even integers$\}$ and it suffices to study the latter set of states.

[‡] In fig. 2 of ref. [11] the labels (n_1, n_2) for the curves marked (12,4) and (8,10) were inadvertently interchanged.

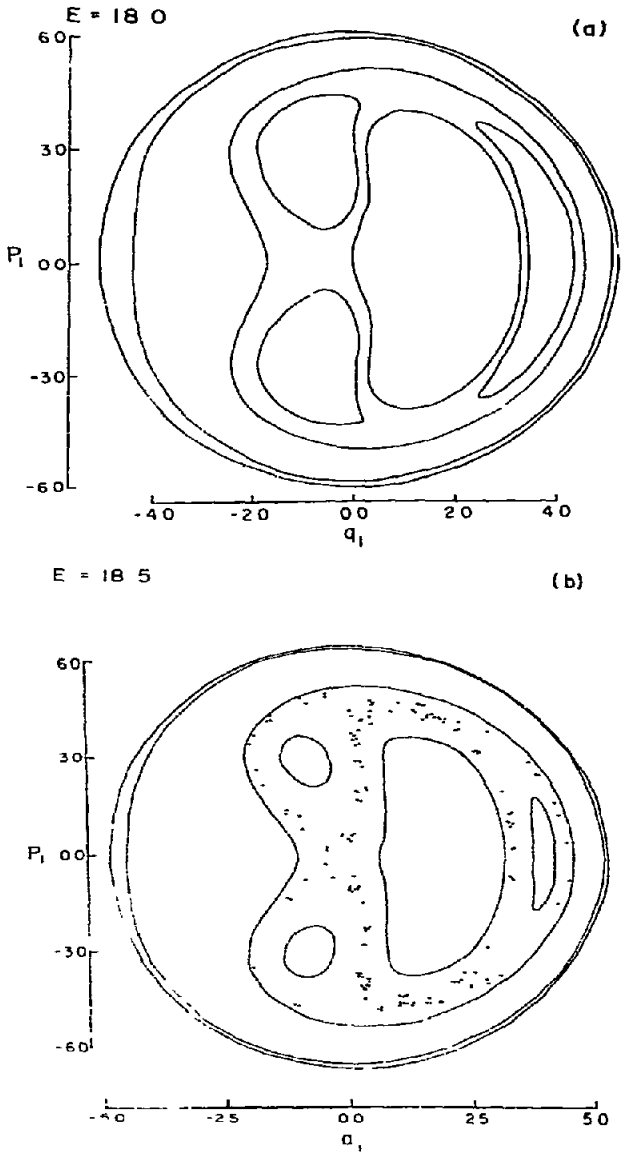

Fig 2 Surface of section of the GHH system for which the action curves are shown in fig. 1, at $E = 18$ units (a) and for $E = 19$ units (b)

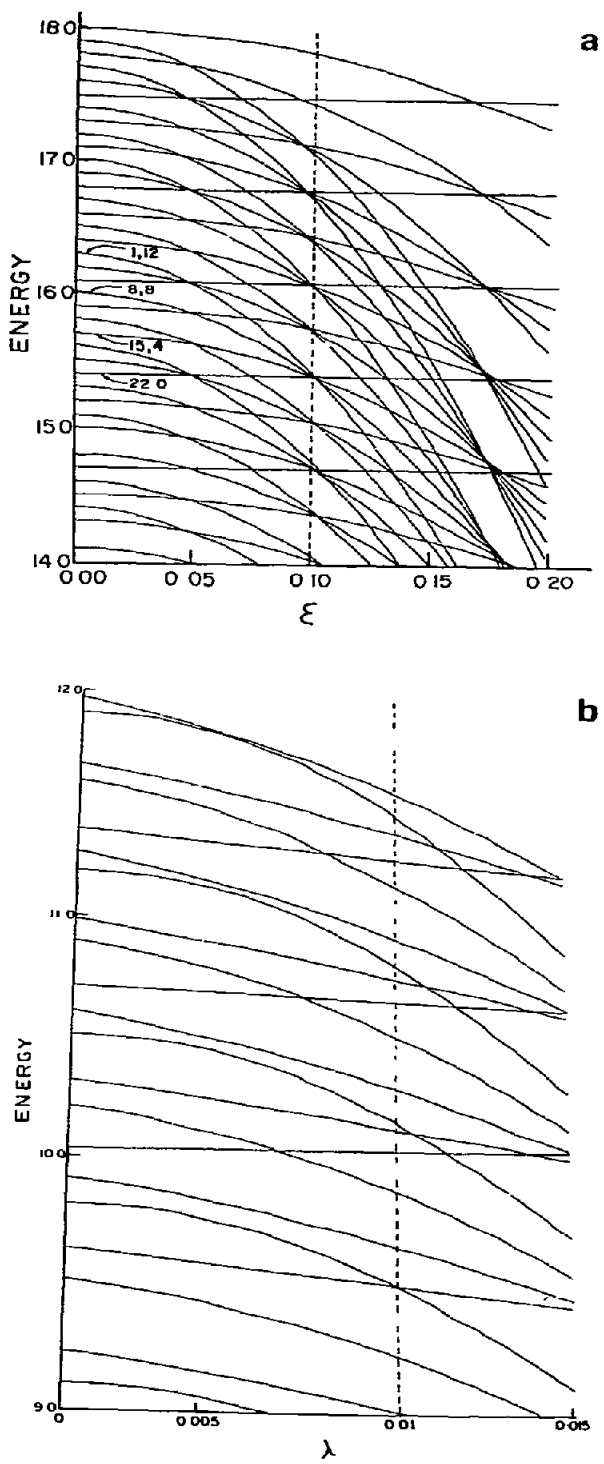

Fig 3 (a) Constant-action curves for the GB system with $\omega_1^2 = 0.49$, $\omega_2^2 = 1.69$, $\chi = -1/2$, $c = 1$, as a function of the perturbation parameter ϵ. (b) With $\epsilon = 0.1$, the further development of the action curves under the effect of the second parameter, λ. To give the appropriate density of states, the unit of action c has been reduced to 0 85.

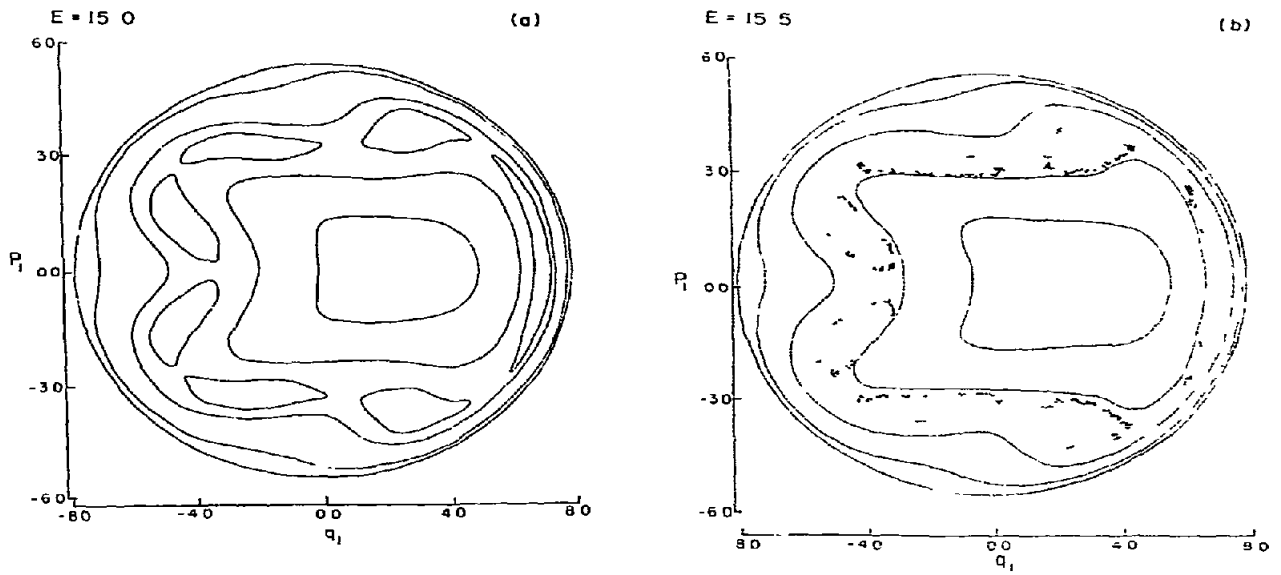

Fig 4. Surfaces of section for the GB system (action curves are given in fig. 3a) at (a) $E = 15$ units and (b) $E = 15.5$ units

be noted that the system is not integrable, and the parameter ratios are not close to the special values when the GHH has the Painlevé property.

First consider the GB system. The dissociation energy is 17.49. The zeroth-order frequencies are in the ratio 7 : 13, which is a high-order resonance. The action curves for $\chi = -1/2$, $c = 1$ are shown in fig 3a, in the energy range $14 \leqslant E \leqslant 18$. What can be noticed is the structure of the avoided crossings around $\epsilon = 0.1$, they occur in well-separated bunches corresponding to $|\Delta n_1| : |\Delta n_2| = 7 : 4$. Due to the large differences in the quantum numbers of the interacting states, one

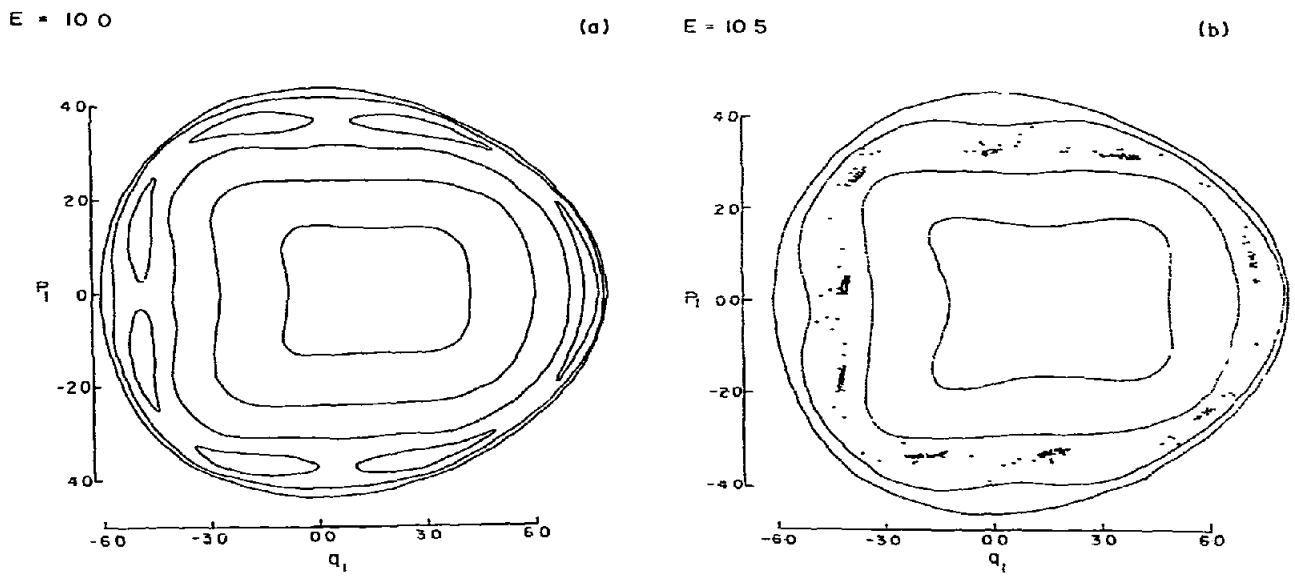

Fig 5 Surfaces of section for the GHH system (action curves are shown in fig. 3b) at (a) $E = 10$ units and (b) $E = 10.5$ units.

expects that these do not have substantial width. The lowest set of crossings centered at $\epsilon = 0.1$ is at $E \approx 15\ 25$, and the prediction therefore is that chaotic motions will become appreciable only around that energy.

When λ is now increased from 0 to 0.01, the dissociation energy is lowered to 11.46 units. To conform to the typical density of states in the previous systems, the appropriate value of c is somewhat smaller, $c \approx 0.85$. With this value of the action unit, the energy curves for $\epsilon = 0.1$ are presented in fig 3b in the range $9 \leqslant E \leqslant 12$ Multiple avoided crossings occur around $E = 10\ 25$ and here the expectation is that appreciable chaos sets in only at this high (relative to dissociation) energy. Interestingly, the curves for $\chi = 0$, $c = 1$, i.e. the quantal states examined in ref [32] show *no* multiple avoided crossings: this is a good example of the regime 1 behaviour discussed in section 2.

Surfaces of section for the GB and GHH systems have been computed and are shown in figs 4 and 5. For the GB system, the surface of section at $E = 15$ displays regular behaviour, while at $E = 15\ 5$, there is evidence of chaotic motion. For the GHH system, the corresponding surfaces at $E = 10$ and $E = 10.5$ indicate the onset of chaos around the latter energy.

As in other similar systems, the extent of classical chaos increases with energy. One can obtain the measure of regular motions from the surfaces of section. This information is summarized in fig. 6, where the fraction of regular regions, the VAK density [6], for the systems examined here is graphed versus the scaled energy, $E/E_{\text{dissociation}}$.

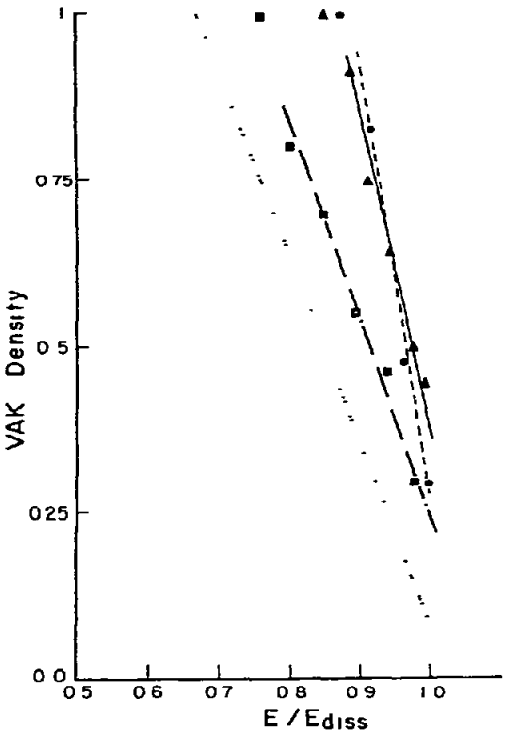

Fig 6 Relative measure of regular motions (the VAK density) for the systems studied here, ■– –■: $\omega_1^2 = 1.6$, $\omega_2^2 = 0\ 9$, $\epsilon = 0.08$, $\lambda = 0\ 01$; ▲–▲ and ●– –● are for $\omega_1^2 = 0\ 49$, $\omega_2^2 = 1\ 69$, $\epsilon = 0.10$, $\lambda = 0$ and $\lambda = 0\ 01$ respectively. For comparison, the corresponding information for $\omega_1 = \omega_2 = 1$, $\epsilon = -1$, $\lambda = 1/3$ (taken from ref [10]) is also shown, ...

4. Discussion

The results presented here, and previous work [11] combine to show the utility of the method of avoided crossings in detecting classical chaos Except for the case of the specific resonances, where the simple perturbation theory breaks down, this method can be applied to a variety of systems; this at least partially bypasses the need for computing large numbers of trajectories. Additional important exceptions are integrable systems, where the method fails entirely, it is to be emphasized that while the eigenvalue spectrum of non-integrable systems show avoided crossings, the reverse of this statement is not, in general, true. Arbitrary integrable systems with any eigenvalue distribution whatsoever can be constructed (specifically, for example, the integrable hamiltonian F given in section 2 will have a spectrum quite similar to that of H). Thus we exclude these cases. This can be done most easily by using the recently developed criterion of the Painlevé property to identify the special values of the parameters when the system becomes integrable [20,30]. At present there is no reasonable way in which the avoided crossings method can itself be used to distinguish between integrable and non-integrable cases

It is greatly desirable to have available a simple reliable method for predicting the occurrence of widespread chaos in molecular systems. On the one hand, it is necessary to know the regime of applicability of

statistical theories which implicitly assume the ergodic hypothesis [33]. On the other hand, the lack of simple classical–quantum correspondence principles for the irregular spectrum [14] is reflected in an inability of quantizing such chaotic motions [14,34].

The method of avoided crossings is essentially an attempt to use the observation that the quantum states associated with classical chaos, the quantum irregular spectrum, show several avoided crossings [9,28,35] rather than degeneracies, as a useful technique by which the onset of classical chaos can be detected This is done in three conceptual steps, by (i) adjusting the size of the unit of action (c or h) to be sensitive to a predetermined minimum measure of chaotic motions, (ii) utilizing the fact that the avoided crossings may be identified by the use of non-degenerate perturbation theory, where they show up as actual crossings [21], and (iii) using a lattice structure in the space of action variables to treat both the quantizable and non-quantizable tori on an equal footing.

The major emphasis in this paper has been in the elucidation of the gross features of the dynamics by simple analytical and graphical techniques We have shown earlier [11] how the irregular regions can be identified, by using perturbation theory to approximately obtain the coordinates of the unstable tori In fact, a semiclassical parameterization of the route to chaos in such systems can be defined by following the development of a torus, with a set of well-defined approximate action variables, under variation of perturbation parameter [36].

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Appendix

The details of the Lie transform [26] are well known and we simply present the results for the canonical transformations

$$F(\xi,\eta;\epsilon,\lambda) = \tfrac{1}{2}[\omega_1^2(\xi_1^2+\eta_1^2/\omega_1^2)+\omega_2^2(\xi_2^2+\eta_2^2/\omega_2^2)]$$
$$+\frac{\epsilon^2}{2\omega_1^2(\omega_1^2-4\omega_2^2)}[(\omega_2^2-3\omega_1^2/8)(\xi_2^2+\eta_2^2/\omega_2^2)^2$$
$$+\omega_1^2(\xi_1^2+\eta_1^2/\omega_1^2)(\xi_2^2+\eta_2^2/\omega_2^2)]$$
$$-(3\epsilon\lambda/4\omega_1^2)(\xi_1^2+\eta_1^2/\omega_1^2)(\xi_2^2+\eta_2^2/\omega_2^2)$$
$$-(15\lambda^2/16\omega_1^2)(\xi_1^2+\eta_1^2/\omega_1^2)^2+\mathcal{O}(\epsilon^4,\lambda^4). \quad (A.1)$$

Transforming to action–angle variables, one obtains

$$K(I;\epsilon,\lambda) = (2\pi)^{-1}(I_1\omega_1+I_2\omega_2)$$
$$+\frac{\epsilon^2}{2\omega_1^2(\omega_1^2-4\omega_2^2)}[(\omega_2^2-3\omega_1^2/8)I_2^2/\pi^2\omega_2^2$$
$$+\omega_1 I_1 I_2/\pi^2\omega_2]-\frac{3\epsilon\lambda I_1 I_2}{4\pi^2\omega_1^3\omega_2}$$
$$-\frac{15}{16}\frac{\lambda^2 I_1^2 I_2^2}{\pi^2\omega_1^4}+\mathcal{O}(\epsilon^4,\lambda^4). \quad (A.2)$$

Finally, imposing the lattice structure (with the unit of action/2π set equal to c) one gets

$$E(n,\chi;\epsilon,\lambda)$$
$$=(n_1+\chi_1+1/2)\omega_1 c+(n_2+\chi_2+1/2)\omega_2 c$$
$$+\frac{2\epsilon^2(\omega_2^2-3\omega_1^2/8)}{\omega_1^2\omega_2^2(\omega_1^2-4\omega_2^2)}(n_2+\chi_2+1/2)^2c^2$$
$$+\left[\frac{2\epsilon^2}{\omega_1\omega_2(\omega_1^2-4\omega_2^2)}-\frac{3\epsilon\lambda}{\omega_1^3\omega_2}\right](n_1+\chi_1+1/2)$$
$$\times(n_2+\chi_2+1/2)c^2-(15\lambda^2/4\omega_1^4)(n_1+\chi_1+1/2)^2c^2$$
$$+\mathcal{O}(\epsilon^4,\lambda^4), \quad (A.3)$$

which gives the "classical eigenvalue" for any set of actions as a function of the parameters. The Maslov indices, α_1,α_2 for this case are both equal to 2.

The perturbation expressions (A.1)–(A.3) are valid as long as $\omega_1/\omega_2 \neq 1$ or 2 within $\mathcal{O}(\epsilon)$, and in the examples treated in section 3, this requirement is satisfied. It may be noted that second-order quantum-mechanical perturbation theory also yields the above expression to within a constant term, $-3\lambda^2/16\omega_2^2(\omega_1^2-4\omega_2^2)$. This correction amounts to less than 0.1% at the energies of the highest bound levels

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