

# On the onset of strong mode coupling in small polyatomic molecules

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(Received 6 July 1982; accepted 18 October 1982)

The number of vibrational states corresponding to separable, quasiperiodic motion of low dimensionality is estimated by a generalization of the analysis of the quantum-mechanical Hénon–Heiles problem by Hose and Taylor. The number of nonseparable states with strongly coupled modes appears to overwhelm the number of separable “quasiperiodic” states whenever the molecule in question contains five or more vibrational quanta, and may dominate for states with four or even three vibrational quanta. Some comments are made to try to clarify the concepts of separability and quasiperiodicity.

Hose and Taylor,<sup>1</sup> in extending the work of Nordholm and Rice<sup>2</sup> on quantum ergodicity, have studied the quantum states of the Hénon–Heiles potential whose energies are below the barrier to dissociation, and have shown how these states can be classified unambiguously (but not necessarily uniquely) into three categories. The categories are the “rotating” quasiperiodic states, the “pendulum-like” quasiperiodic states, and the other states, which are not quasiperiodic and are presumably chaotic in some sense. The first two categories are called  $Q^I$  and  $Q^{II}$  states by Hose and Taylor,<sup>1</sup> and are distinguished respectively by the criteria that a  $Q^I$  state has a wave function that is more than 50% made up of an eigenfunction of the uncoupled isotropic harmonic oscillator contained in the Hénon–Heiles Hamiltonian, and that a  $Q^{II}$  state has a wave function composed of more than 50% of an eigenfunction of the uncoupled two-dimensional harmonic-plus-anharmonic oscillator contained in the Hénon–Heiles Hamiltonian. Some states near the bottom of the potential satisfy both criteria; most satisfy only one or the other, or neither. This is an extension and quantification of the idea put forward by Nordholm and Rice,<sup>2</sup> that simple quasiperiodic motion is associated with dominance of a single eigenstate, and that lack of dominance of a single eigenstate is associated with “chaos,” “ergodicity,” or “strong mode coupling.”

The idea is current that a real system could exhibit states that correspond closely to different approximations to its true Hamiltonian and hence to different approximate constants of the motion. The tetragonal, trigonal, and diagonal distorted octahedra described by Harter, Patterson, and de Paixao<sup>3</sup> is one example, in which the exact dynamics are described by a Hamiltonian which is approximately that of a spherical top. Another example is the local mode representation,<sup>4–6</sup> which successfully describes a small subset of the manifold of excited vibrational states of molecules such as H<sub>2</sub>O or UF<sub>6</sub>. Still another example, this time from theory, is the model used by Natanson, Amar, and Berry<sup>7</sup> to represent the melting of small clusters as the transition, for a cluster of  $N$  identical particles, between a state appropriately represented by a rigid-rotor, small-amplitude vibrator Hamiltonian and a state represented by the Hamiltonian of a nonrigid cluster held together by pairwise attractions.

Here, we shall show how the insights revealed by the Hose–Taylor analysis can be extended generally to real molecular systems; how that extension can be put to practical use for constructing approximate density-of-state functions for the rovibrational states of some kinds of polyatomic molecules and homonuclear clusters, and how one may estimate the fraction of the total number of states for which the motion in the classical analog is quasiperiodic, as the number of vibrational quanta is increased. The concept of quasiperiodicity is readily linked to the separability of the quantum equations of motion. We make *no* attempt here to perform the converse association, of inseparability of the quantum equations with classical chaos.

The motivation for this work is to help clarify the distinctions between excited states relevant to a particular process, such as absorption of dipole radiation or intramolecular energy transfer or inelastic electron scattering, and the entire manifold of excited states that determines the thermodynamic properties of a molecule. It seems to be suspected, increasingly, that the process of absorption or emission of electric dipole radiation involving highly excited vibronic states is dominated by states whose classical counterparts involve quasiperiodic motion in one or possibly two dimensions. Certainly the mechanical picture of the coupling of bound electrons with a uniform electric field, linearly, elliptically or circularly polarized, almost forces one to that expectation. Proving this belief is a task for the future. Meanwhile, we address one step toward the larger problem and show what proportion the states associated with separable, quasiperiodic motion in one or two dimensions constitute in the total density of states.

First we write the formal exact Hamiltonian for our system of several degrees of freedom as decomposable in more than one way:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_A^0 + \mathcal{H}'_A \\ &= \mathcal{H}_B^0 + \mathcal{H}'_B .\end{aligned}$$

Each  $\mathcal{H}_K^0$  is assumed to be *separable* in some coordinate systems. For the Hénon–Heiles system, Hose and Taylor took two forms of the zero-order separable Hamiltonians, corresponding to

$$\mathcal{H}_A^0 = T(r, \theta) + 1/2r^2,$$

$$\mathcal{H}_A' = \frac{\lambda r^3}{3} \cos 3\theta,$$

and

$$\mathcal{H}_B^0 = T(x, y) + 1/2(x^2 + y^2) - \frac{\lambda x^3}{3},$$

$$\mathcal{H}_B' = xy^2.$$

Here  $T$  is the kinetic energy. (Strictly, Hose and Taylor used a projected effective Hamiltonian but that point is not relevant at this stage of our discussion.) The eigenfunctions of  $\mathcal{H}_K^0$  satisfy

$$\mathcal{H}_K^0 \psi_i^K = E_{K,i}^0 \psi_i^K,$$

and presumably form complete sets. The eigenfunctions of  $\mathcal{H}$  satisfy

$$\mathcal{H} \psi_j = E_j \psi_j,$$

$$\psi_j = \sum C_{ji}^K \psi_i^K, \quad K = A, B, \dots$$

The eigenfunctions  $\psi_i^A$  and  $\psi_i^B$  correspond to states of separable Hamiltonians with quantum numbers  $i, \alpha, \beta, \dots$ ; e.g., with  $\mathcal{H}_A^0$ ,  $l$ , and  $m$  are good quantum numbers, while with  $\mathcal{H}_B^0$ ,  $n_x$ , and  $n_y$ , the number of oscillator quanta in the anharmonic ( $x$ ) and harmonic ( $y$ ) oscillators, are good quantum numbers.

An analog to the Hose–Taylor decomposition and classification exists for molecular motions. This is the procedure of casting the exact Hamiltonian in forms appropriate to various approximate quantizations; the procedure takes different forms according to the problem. One example is the use of the various Hund's cases of rotational coupling; another is the representation of the triatomic system as a conventional rigid-rotator, small-amplitude vibrator, as a diatomic undergoing hindered rotation in the field of a close neighbor or as a diatomic rotating freely in the field of a weakly interacting third atom.<sup>8</sup> The examples on which we shall draw most heavily are those of clusters of three, four or five identical particles for which the zero-order Hamiltonians may be taken as any conventional molecular structure or as a nonrigid cluster. Energy level correlation diagrams have been worked out for these and for the linear  $XYX$  system and the  $XY_5$  six-body system, which we shall use in our development.<sup>9–12</sup>

The quasiperiodic eigenfunctions obtained by Hose and Taylor tend, particularly as the energy increases, to correspond to the most lopsided of the possible distributions of quanta. That is, the  $Q^I$  quantum states corresponding to classical orbiting states are states in which all the quanta or all the quanta but one are in one of the angular momentum components  $+l$  or  $-l$  of the isotropic oscillator. Most of the  $Q^{II}$  quasiperiodic quantum states corresponding to pendulum-like oscillations have all their quanta or all but one of their quanta (for six or fewer quanta) in the anharmonic oscillator. This is meant in the sense that the single  $SU(2)$  state comprising over 50% of the accurate  $Q^I$  eigenfunction is most commonly a state with  $m_1 = +l$

or  $-l$  or with  $m_1 = l-1$  or  $-(l-1)$ , and that the principal contributor to a  $Q^{II}$  eigenfunction with  $n$  quanta is a state with  $n_x = n$ ,  $n_y = 0$ , in most cases.

We further note, following Hose and Taylor, that the  $Q^I$  and  $Q^{II}$  states but not the "chaotic" states can be generated by the imposition of quantum conditions on quasiperiodic classical trajectories.<sup>13,14</sup> It is not particularly relevant here whether one uses the approximate methods of Heller<sup>14</sup> or the more accurate methods of Marcus, Noid *et al.*<sup>13</sup> What is important is that one subset of quantum states can be determined by an efficient procedure that not only locates the state, but also reveals what its near constants of the motion are. This procedure by itself does not locate all the states, or, most probably, even a majority of them, but it does establish labeled pegs on the energy scale, *corresponding to the ways the real system may fall almost into the pattern of some simple  $\mathcal{H}_K^0$ .*

Our next step is simply to incorporate this information into the energy level correlation diagram that includes as its limits all the  $\mathcal{H}_K^0$ 's revealed by the quasiperiodic motions. We begin with the question "How are the quasiperiodic and chaotic states distributed in the range of bound or quasibound states?" We now break that question into two parts. First, we ask how the quasiperiodic states are distributed, and then ask how the other states are distributed among the quasiperiodic levels. We assume that the first question is already answerable, at least in principle, by the semiclassical methods. It is the second question we address here: we suppose we may identify the states corresponding to "maximally lopsided" quantization with quasiperiodic states of classical motion, and then ask how the other states may be expected to be distributed with respect to those quasiperiodic states.

Before attempting to answer our new question, we comment on the nature of the two categories of quantum states. The set we have called "quasiperiodic," following the usage of Hose and Taylor, really comprises states for which the Hamiltonian is approximately separable, so that the corresponding classical motion is quasiperiodic *in a space of low dimensionality*. This means that a torus or a vague torus<sup>15</sup> exists for the analogous classical trajectory, and that the quasiperiodicity is thereby confined to such a low dimensionality that we can readily recognize it. The other states are called chaotic by Hose and Taylor. These authors are careful to distinguish their usage from the specific mathematical sense of exponentially diverging trajectories but seem, by their choice of the term, to feel that some association of the ideas might be made. We prefer to avoid the term "chaotic" at this stage. Rather, we can use a term that recognizes a more readily established property of the "nonquasiperiodic" quantum states, namely their *nonseparability*. The states that do not correspond to maximally lopsided quantization are states for which the Hamiltonian is presumably nonseparable, or for which all or most of the internal modes of motion are coupled. Hence the trajectory of a classical state analogous to a nonseparable quantum state pursues a path in  $3N-6$  dimen-

sions in the translating, rotating frame of an  $N$ -atomic molecule. These are states in which the modes of internal motion are strongly coupled. We shall suppose that there is no magic "hidden separability" for these states, excepting a possible tiny pathological subset.

Note that separability or approximate separability here is not intrinsic to the full Hamiltonian in isolation. It is best to look upon the kind of separability we consider here as a property of the Hamiltonian together with its eigenvalues. For some eigenvalues, the full Hamiltonian is approximately separable in one way; for other eigenvalues it is approximately separable in another way; for many eigenvalues, the Hamiltonian is not approximately separable at all. Moreover the eigenvalues corresponding to one particular separation may be relatively confined to an energy band of their own, as with the normal mode separation value for low quantum numbers, or they may be interspersed with eigenvalues associated with another separation and with the nonseparable states, as in the quasibound states of the Hénon–Heiles potential, or the local stretching mode states of water or benzene. This kind of eigenvalue-dependent separability must be distinguished from cases in which some exact integrals of motion exist.

The relation between chaos and nonseparability is unknown. It is tempting to suppose that each exact nonseparable eigenstate of vibrational motion of an  $N$ -atom polyatomic molecule corresponds to a closed classical trajectory in a  $(3N-6)$  or perhaps  $(3N-3)$  dimensional space, that such a trajectory satisfied a quantized action principle, and that the other classical trajectories of the same and approximately the same energy diverge from the "quantum trajectory" in the exponential manner associated with chaos in its strict sense. Until these suppositions are proven or disproven, we prefer to reserve the term "chaos" for classical systems and to use "separable," "approximately separable" and "nonseparable" for quantum systems. The success of the Hose–Taylor analysis in associating approximately separable quantum states with quasiperiodic classical states is such a powerful step that we do allow ourselves to use the terms "approximately separable" and quasiperiodic interchangeably to mean approximately separable into one or two degrees of freedom and quasiperiodic in one or two dimensions.

### THE $X_3$ , $X_4$ , and $X_5$ molecules

We suppose that the  $X_3$  molecule of interest has an equilibrium geometry (three equivalent geometries if this form has symmetry lower than  $C_{3v}$ ), around which the rovibrational ground state is localized.

The lowest states are presumably near rigid-rotor states of rotational excitation. The first states for which the question of quasiperiodicity or chaos must correspond to at least one quantum of vibrational excitation.

For the  $X_3$  system, there are at least two approximate  $\mathcal{H}_K^0$ 's we might choose: that of the equilateral triangle and that of a completely nonrigid object. The

former has the three rotational degrees of freedom of a symmetric top and three vibrations: a totally symmetric dilatation and a doubly degenerate  $E$  mode carrying a quasiangular momentum. It is natural to suppose that there are some levels for which rotations and vibrations are separable enough to allow those levels to be assigned separable quantum numbers  $N$  and  $K$  for rigid-body rotation, either  $n$ ,  $l$ , or  $n_+$ ,  $n_-$  for the doubly degenerate vibration and  $n_s$  for the symmetric stretch or dilation mode. In this range of energy, where the spacings of the rigid symmetric top levels are small compared with the splittings of the vibrational levels, the states exhibiting quasiperiodic motions will surely include those with  $l = n$ , i. e., with the maximum quasiangular momentum; these are precisely analogous to Hose and Taylor's  $Q^J$  states. We should also be prepared to find quasiperiodic motion associated with states in which all the quanta are in the dilatation. And of course the separable rotations are automatically periodic. We can thus enumerate the states we expect to be quasiperiodic in the total level pattern for the equilateral-triangular molecule. The number of such quasiperiodic states, for any level with  $\alpha$  vibrational quanta and no rotation is three, if we only admit the most extremely lopsided allocation of quanta. If we allow one quantum to be in another mode, the number of quasiperiodic states goes up to nine, for any total number of vibrational quanta  $\alpha$ . Beginning at the level of three or more vibrational quanta, we expect that the other states will not conform to any low-dimensional, separable periodic motion or any single separable basis state of the Hamiltonian of the equilateral triangle.

In this example, it is not obvious what the naturally periodic modes of the nonrigid system will be, in simple mechanical terms. However we can expect that if we use as our model for this limit the six-dimensional isotropic oscillator, that in the  $\nu$ th set of states, those in which all the  $\nu$  quanta are in one mode are the ones likely to be quasiperiodic. That is, we can expect of order *six* states at each level to exhibit quasiperiodic motion. If we include states with all the quanta but one in a single mode, this number goes up to 36. The degeneracy of the level of the six-dimensional isotropic oscillator with  $\nu$  quanta is

$$g_\nu = \frac{(\nu + 5)!}{\nu! 5!},$$

corresponding to 1, 6, 21, 56, 126, 353, 462, 792, and 1287 for  $\nu = 0$  through 8.

This picture tells us that for the three-body system with two  $\mathcal{H}_K^0$ 's, we may expect the quasiperiodic states to number as few as nine if only the extremes of lopsided allocations of quanta are counted, or as many as 45, if one quantum may be in some mode other than the one with maximum excitation. The appearance of what Hose and Taylor called chaos—i. e., the onset of a predominance of nonseparable states corresponding to no simple, low-dimensional mechanical motions—sets in very quickly, at the level of three or four quanta in the quantization appropriate to either the rigid or the nonrigid limit. Without specification of the ratio of

mean vibration frequency to rotational constant for the rigid limit, one cannot specify precisely where this will occur. If one supposes that strong mode coupling in the rigid limit is restricted to vibrations, then the relevant degeneracy is only that of the three vibrations and we can use the totally symmetric representations of  $SU(3)$ , namely,

$$g_\nu = \frac{(\nu + 2)!}{\nu! 2!}$$

or 1, 3, 6, 10, ... to estimate this degeneracy. Moreover, in this case, probably only the two local stretching modes will be quasiperiodic in high excitation, so we can expect chaotic behavior here at about the level of four vibrational quanta also.

In the case of the four-body problem, we have more options for the simple mechanical motions, corresponding to various alternative limits and to their respective  $\mathcal{H}_K^0$ 's. One can imagine, for example, local bond stretching motions and the pseudoangular momentum of the tetrahedral molecule and the internally rotating double diatomic as two consistent approximate  $\mathcal{H}_K^0$ 's in addition to the nonrigid limit. Here, the number of presumably quasiperiodic, simple mechanical motions of the tetrahedron is of order six, and of the double diatomic, about five (doubly degenerate internal rotations with all the rotational quanta in one diatomic, and the diatomic-diatom stretch). Add perhaps two for overall rotation with maximum  $M$  and we get about 12 to 14 modes that we may expect to be quasiperiodic. The total degeneracy of this system goes up (for the nonrigid limit, but again the magnitudes, carry over to the rigid rovibrator) as

$$g_\nu = \frac{(\nu + 8)!}{\nu! 8!}$$

or 1, 9, 45, 165, ... In this case we can expect nonseparable behavior in most states beginning with about *three* vibrational quanta.

For five or more atoms, we may estimate the number of quasiperiodic states as follows. For a nonrigid  $N$ -atom molecule, the upper bound on the number of kinds of quasiperiodic internal motions is the number of internal modes  $3N-3$ . Hence, if we count as periodic the states with all or all but one of the quanta in a single mode, the quasiperiodic or separable state number at most  $(3N-3)(3N-4)$ . For a rigid molecule of  $N$  atoms, with  $3N-6$  vibrations, the number of states of separable motion would be  $(3N-6)(3N-7)$ . The number of ways a full Hamiltonian might be expected to break into zero order and perturbation parts must be between one and roughly  $N$ , at the uppermost. Hence the number of separable states must lie between  $(3N-6)$  (if the system is rigid, has only one zero-order approximation and all the quanta must be in one mode to give separability) and the approximate upper bound of  $(3N-3)(3N-4) + N(3N-6)(3N-7)$ . The most important thing about this number is that it depends on the number of degrees of freedom but not on the number of quanta.

The onset of the dominance of nonseparable states occurs when the total number of states with a given num-

ber of quanta is larger than the possible number of separable states. If we count the number of states by including all motions except the center-of-mass translations, then there are  $3N-3$  degrees of freedom and

$$g_\nu = \frac{(\nu + 3N - 4)!}{\nu! (3N-4)!}$$

states with  $\nu$  quanta, if the  $(3N-3)$ -dimensional isotropic oscillator model is used to count the states. If we exclude rotations but again estimate on the basis of the isotropic oscillator,  $g_\nu$  becomes  $(\nu + 3N-7)!/\nu!(3N-7)!$ .

Where does the onset occur for the dominance of nonseparable states? A quick computation shows that in the least quasiperiodic situation, with only  $3N-3$  quasiperiodic states and  $(\nu + 3N-4)!/\nu!(3N-4)!$  states of  $\nu$  quanta, the nonseparable states dominate when  $\nu \geq 3$ . In the other extreme case, with  $(3N-3)(3N-4) + N(3N-6)(3N-7)$  quasiperiodic states and only  $(\nu + 3N-7)!/\nu!(3N-7)!$  for the total number of relevant states of  $\nu$  quanta, we find that for  $N = 5$ ,  $N_{\text{quasiperiodic}} = 492$ , there are 495 states with  $\nu = 4$  and 1287 states with  $\nu = 5$ . For  $N = 6$ ,  $N_{\text{quasiperiodic}} = 1002$ , there are 1365 states with  $\nu = 4$  and 4368 states with  $\nu = 5$ . For  $N = 7$ , there are 1776 quasiperiodic states counted as we do here, 3060 states with  $\nu = 4$  and 11 628 states with  $\nu = 5$ . In other words, however we estimate the numbers of states and quasiperiodic states, the nonseparable states dominate the total density of vibrational states whenever the system contains five or more vibrational quanta, and most tend to be comparable in number to the separable states, for states with four quanta, unless the tendency toward quasiperiodic behavior corresponds to the most extreme model just used above. This result is the consequence of the dominance of the factorial growth of the density of states over the power-law dependence of the estimated number of separable states.

This approach must be used with some caution. We do not wish to imply that the chaos as used here has anything to do with the rate of divergence of classical trajectories; it may or may not. Moreover, we also do not wish yet to speculate on the question of intensities of transitions to these separable, quasiperiodic states, although it is tempting to suppose that they are the states carrying most of the oscillator strength. All we can claim here is to see a strong indication of where complicated or chaotic motions begin to be important in the spectra of polyatomic molecules, and what considerations give rise to that condition.

#### ACKNOWLEDGMENT

This research was supported under a Grant from the National Science Foundation.

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