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VIBRATIONAL MOTION IN THE REGULAR AND CHAOTIC REGIMES, CLASSICAL AND QUANTUM MECHANICS

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INTRODUCTION

There are many experiments which are related to intramolecular energy transfer. Initially, they involved primarily thermal unimolecular reactions[1] and chemical activation.[2] More recently, experiments which are more state-selective have also been performed in which one zeroth order mode (e.g., some bond or normal mode) has been excited. These experiments include infrared multiphoton absorption,[3] reactions induced by excitation of high CH overtones,[4] dissociation of vibrational state-excited van der Waals' complexes,[5] and fluorescence spectra from mode-selected vibrationally-excited substituted aromatic molecules.[6]

Paralleling the experiments has been considerable theoretical interest in the subject of intramolecular energy transfer ('randomization'). In the present article some recent studies of our group on semiclassical and quantum behavior of states of simple systems are described. These studies were initially for systems with few degrees of freedom, but related concepts are expected to apply to larger systems. A more detailed review of this work and of that in other laboratories will appear elsewhere.[7]

CLASSICAL MECHANICS

There have been major developments in the classical mechanics of coupled anharmonic oscillators (and other coordinates) and so applicable to molecular vibrations. In particular, Poincaré speculated around the turn of the century that there were three regimes for the motion of classical mechanical system--one where the classical motion is largely 'regular', one where the motion is both

regular, or for different initial conditions, chaotic, and the third where the motion is largely chaotic.[8]

More recently, in the middle 1950's and early 1960's the famous Kolmogorov-Arnold-Moser theorem (KAM) was developed.[9] It was shown there that at very small values of the perturbation parameter (small perturbation from an 'integrable' system), the motion is 'regular' for almost all initial conditions: i.e., for almost all initial conditions it has m good action variables for a system with m coordinates. Numerically calculated trajectories for coupled anharmonic oscillators have revealed that most initial conditions yield this regular motion even at larger perturbations, but that at still larger ones (or at still higher energies) the classical motion becomes chaotic (or, as it is sometimes called, stochastic, ergodic, irregular) for an increasing fraction of initial conditions.[10]

As a consequence of having these m good action variables, regular motion is expressible in a Fourier series having at most m fundamental frequencies, plus combinations and overtones, and is, thereby, 'quasi-periodic'.[9] A test for finding if the motion is quasi-periodic or if it is, instead, chaotic is given by numerical (computer) experiments in a variety of ways, such as linear instead of exponential separation (in time) of two neighboring trajectories,[11] the pattern of the Poincaré surfaces of section discussed later,[10] and the power spectrum for the trajectory,[12] which has lines corresponding to the above fundamentals, overtones and combinations for a quasi-periodic motion, or has, instead, 'broadened' bands (many lines) for chaotic motion.[12]

The implications of a quasi-periodic behavior for chemistry, in those cases where classical mechanics is a useful first approximation, are several fold. For example, a quasi-periodic trajectory winds itself around a manifold of m-dimensions in a 2m dimensional phase space, namely around a 'torus'. A chaotic trajectory tends, instead, to occupy all of phase space that is not preempted by the tori and that is consistent with the given energy and angular momentum. Thus, only in the chaotic case does the time average of any property calculated from the trajectory tend to become approximately equal to the microcanonical phase space average for the given angular momentum. The restriction, instead, to an m-dimensional torus in a 2m-dimensional phase space involves a considerable confinement of the quasi-periodic trajectory in this phase space. Different theories of unimolecular reactions have been based on these two extremes.[7] Again, the regularity of the vibrational spectrum is expected to more readily permit a coherent absorption of infrared photons than the chaotic case, with its more complicated spectrum. Distinguishing a chaotic spectrum from a quasi-periodic one in the case of molecules with many coordinates may nevertheless be difficult.

Classical quasi-periodic states of motion are of two kinds:[7] those which do not extensively mix the energies of some choice of zeroth order modes and those which do, though in a nonchaotic way. These two types of quasi-periodic trajectories are obtained using, for example, a Hamiltonian frequently employed in nonlinear dynamics studies:

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x(xy + \eta x^2) \quad . \tag{1}$$

Hamilton's equations of motion are integrated numerically. In Figure 1 y(t) is plotted vs. x(t) for the case where ω_x and ω_y are incommensurate.[13,14] An example is given in Figure 2 for the case[15] of $\omega_x = \omega_y$ and in Figure 3 for the case[16] of $\omega_x = 2\omega_y$. All of these trajectories are quasi-periodic.

There is clearly a considerable difference between Figure 1 on the one hand and Figures 2 and 3 on the other. In Figure 1 the amplitude of the y-motion is approximately independent of the x-coordinate and vice versa. I.e., in this quasi-periodic state of the system, there is relatively little mixing of the energy of the zeroth order modes (the x and y modes) during the motion, because the unperturbed frequencies are incommensurate. In contrast, in Figure 2, which has a 1:1 resonance, the motion is sometimes along the x-direction, sometimes along the y-direction, and sometimes in between. I.e., even in this quasi-periodic state there is extensive modal energy mixing. Figure 3 is intermediate; there is a higher order resonance, and so the system has some but a more limited modal energy mixing than that in Figure 2. Thus, modal energy mixing does not itself imply classical chaos, since it does occur in quasi-periodic states--those with zeroth order internal resonances--as well as in chaotic states. Indeed, for the system in Figure 2 the distribution of the internal angular momentum

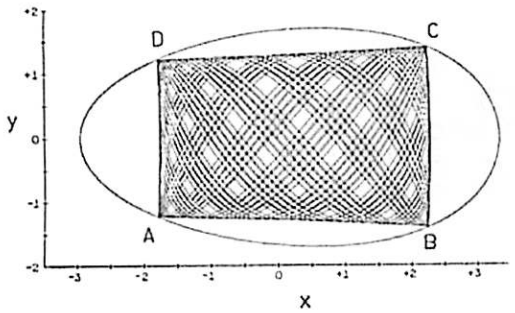

Fig. 1. A quasi-periodic trajectory for Eq. (1) with ω_x and ω_y incommensurate.

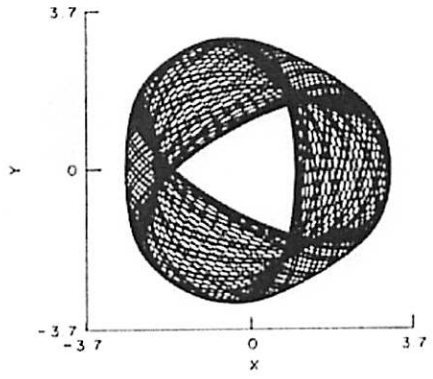

Fig. 2. A quasi-periodic trajectory for Eq. (1) with $\omega_y = \omega_y$.

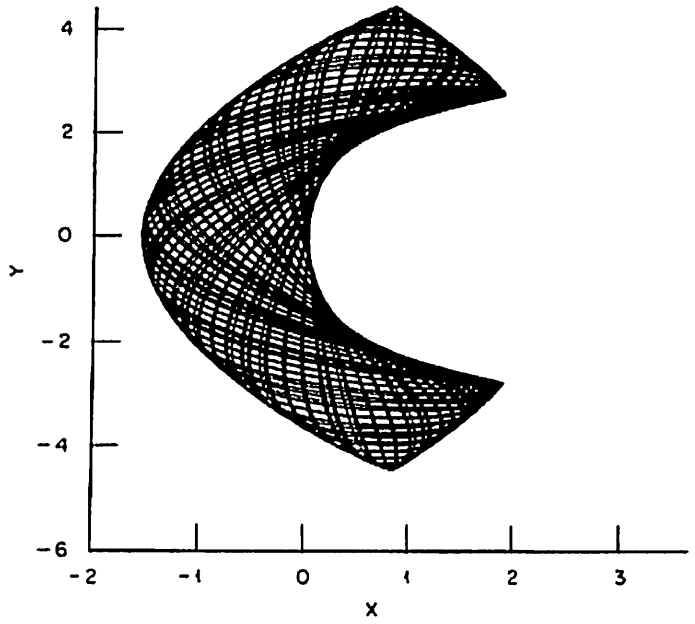

Fig. 3. A quasi-periodic trajectory for Eq. (1) with $\omega_x = 2\omega_y$. Plot of y(t) vs. x(t).

$(yp_x - xp_y)$ is quite nonchaotic. This point has frequently been overlooked in the literature. An example of a chaotic trajectory[16] for a 2:1 resonant system is given in Figure 4. The trajectory is trying to occupy all of the energetically accessible phase space. There is none of the structure of caustics evident in Figures 1-3.

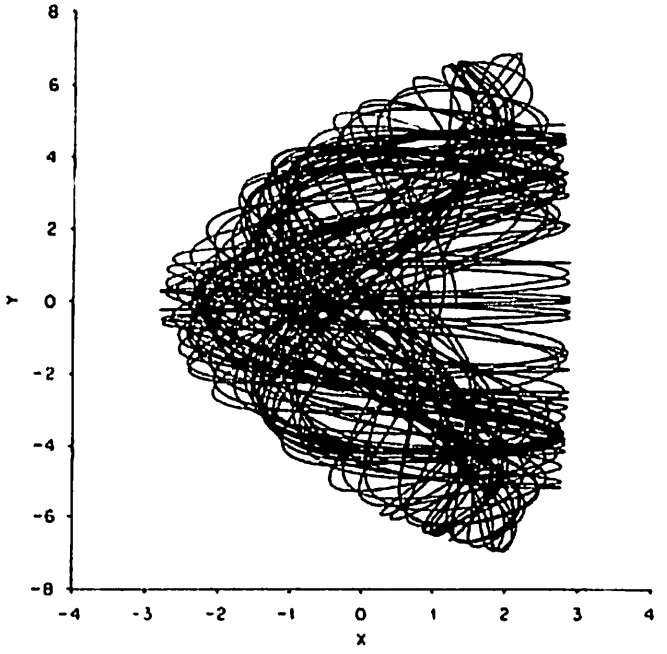

Fig. 4. A chaotic trajectory for Eq. (1) with $\omega_x = 2\omega_y$. Plot of y(t) vs. x(t).

SEMICLASSICAL MECHANICS

We turn next to the corresponding semiclassical version of the quantum mechanical behavior. Using semiclassical arguments it has been possible to calculate from classical mechanics the quantum mechanical energy eigenvalues. The first successful technique for smooth potentials[13] employed exact classical trajectories. The integrals in the left hand side of the semiclassical Eq. (2) were evaluated for coupled anharmonic oscillators.

$$\oint_{C_i} \sum_j p_j \, dq_j = (n_i + \tfrac{1}{2})h \qquad (i = 1 \text{ to } m) \quad . \qquad (2)$$

$\oint$ is a cyclic integral (an integral over a closed path); j goes from 1 to m. For a system of m oscillators there are m topologically independent closed paths C_i, and there are m integers n_i. The left hand side of Eq. (2) is the i'th action variable. We evaluated each of these action variables for m = 2 by choosing the C_i to be the caustics (e.g., the boundaries AB and back, and BC and back, in Figure 1). The initial conditions, including the energy, were then adjusted until the two n_i's calculated in Eq. (2) after evaluation of the left hand sides (m = 2) were integers. The method gave good agreement with the quantum mechanically calculated eigenvalues[13] of the Hamiltonian in Eq. (1).

This method was then extended by choosing each C_i to be a curve (a series of points) appearing in a Poincaré surface of section.[14] In a system of two coordinates (x,y) one plots p_y vs. y for a trajectory each time a trajectory passes some value of x, e.g., x = 0, with $p_x > 0$. A typical plot for several trajectories is given in Figure 5. The area under a curve for one of them gives one of the

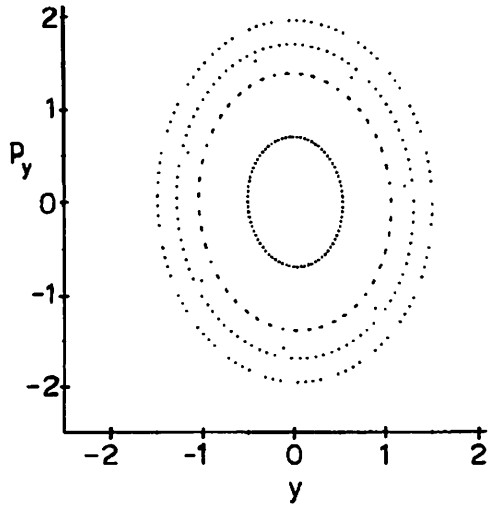

Fig. 5. Example of a surface of section at x = 0 for several trajectories, each typically of the form in Figure 1.

integrals over C_i, while the plot of p_x vs. x at some y gives another topologically independent integral. Once again, good agreement was obtained for the eigenvalues both with the first method and with the quantum mechanical ones.

The integral in Eq. (2) for Figure 4 is independent of the plane (x = a constant) chosen for the surface of section, as long as this plane cuts the same caustics (e.g., AB and DC in Figure 1), and an analogous remark applies to the integral for the other Poincaré surface of section. The method has since been extended to treat systems with zeroth order internal resonances $\omega_1:\omega_2$ = 1:1, 1:2, by introducing curvilinear coordinates.[17] The method cannot be used in the classically chaotic regime: the surface of section has a 'shotgun' pattern there. Indeed, the good action variables in the left hand side of Eq. (2) do not appear to exist there.

The method has been supplemented by a variety of approximate classical techniques, perturbative, perturbative-iterative and variational (reviewed in Ref. 7). In general these methods and the exact trajectory method are complimentary: the former (at least methods involving iteration) require more complicated computer programs but, at least for polynomial potentials, are computationally faster than the trajectory method. On the other hand, the small divisor problem causes perturbation methods ultimately to diverge.[18] The trajectory method provides direct information on the shape of the tori, information which can also be used to introduce appropriate coordinate systems for use with the approximate methods. Approximate techniques are essential for treating large systems, but problems of convergence may appear.

These methods are, like the exact trajectory method, strictly applicable for calculating quantum mechanical eigenvalues only when good action variables, the left hand sides of Eq. (2), actually exist. In the classically chaotic regime they appear not to exist, except for isolated residual families of tori, and some additional method or approximation is needed. In the perturbative-type methods good action variables are assumed to exist, even in the chaotic regime, and Eq. (2) is then used.[19] Thus far, however, this method has not yet been applied to what are called later in this paper quantum mechanically chaotic systems. There is reason to believe that these approximations will break down for such systems,[7] although they may capture certain features. Another possible method, one involving families of periodic systems,[20] has not yet been applied to systems of coupled anharmonic oscillators in either the classically or the quantum mechanically chaotic regimes.

Comparisons between semiclassical and quantum mechanical results have also been made by the spectral trajectory method, and in the classically quasi-periodic regime they show good agreement for both the positions of the spectral lines and their intensities

(fundamentals and overtones) when use is made of the correspondence principle.[12] Once again, much less is understood about the relationship between exact quantum and classical spectra in the classically chaotic regime. Examples of the spectrum for the quasi-periodic and the chaotic trajectories in Figures 3 and 4 are given in Figures 6 and 7, respectively.[21]

QUANTUM MECHANICS

We have compared above the eigenvalues and the spectra, semiclassical with quantum. One can also compare a wavefunction with the trajectory which, by obeying Eq. (2), corresponds semiclassically to it. The quantum mechanical wavefunction ψ corresponding to Figure 3 is given, in the form of $|\psi|^2$, in Figure 8.[16] The base of the former has the same shape as the region occupied by the trajectory for this 2:1 Fermi resonant system.

The relation between classical and quantum behavior in the classically chaotic regime is only beginning to be understood. For example, we studied, for a particular value of λ, the 'Henon-Héiles' system (Eq. (1), with $\omega_x = \omega_y = 1$ and $\eta = -1/3$). We found that the quantum mechanical spectrum reflected regular spacings in the sequences of eigenvalues, even when the classical spectrum was 'chaotic', in the classically chaotic energy regime.[22] Thus, classical chaos is not a sufficient condition for quantum chaos (cf. also Ref. 23). The occurrence of classical chaos arises, according to Chirikov's and Ford's theory,[24] when there are

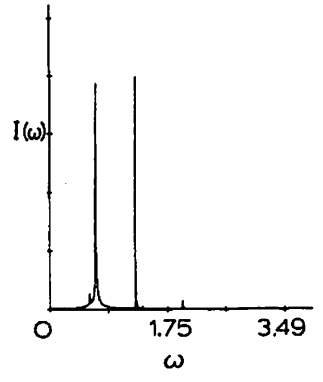

Fig. 6. Spectrum of a trajectory similar to that in Figure 1.

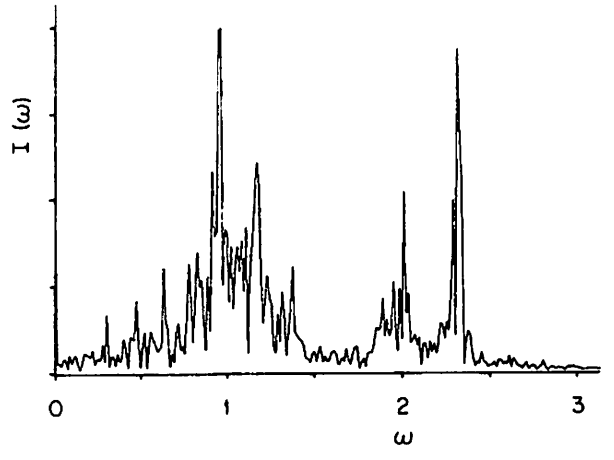

Fig. 7. Spectrum for the trajectory in Figure 4.

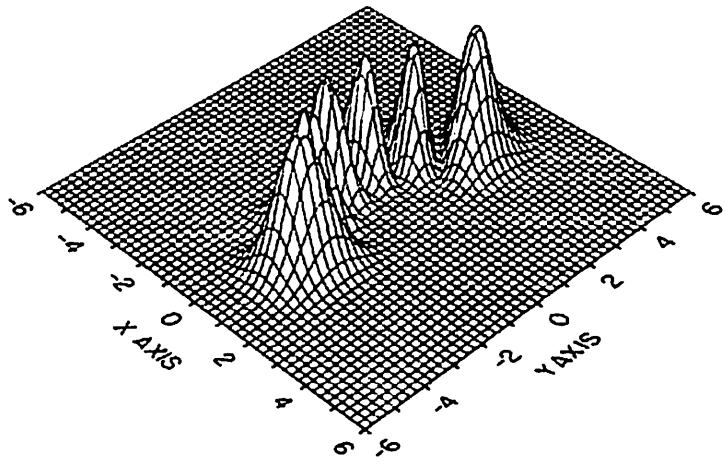

Fig. 8. A wavefunction in the quasiperiodic region, corresponding to the trajectory in Figure 3.

overlapping internal classical resonances. Each resonance has a center and a 'width'. When these widths overlap classical chaos begins.[24] However, when each width contains essentially no quantum states, each classical resonance has no quantum mechanical counterpart, and so the overlap has none either.[25,26] Only when the spacing of the quantum states in the region near the resonant centers is small enough will, by this argument, classical chaos imply quantum chaos for a quantum state. Conditions which can be tested have been suggested.[25,26] Some test of Ref. 25 has been made by Kay.[23]

Information about quantum mechanical resonances, which are expected to cause quantum mechanical chaos (e.g., quite uneven spacings in eigenvalue sequences), particularly when the resonances 'overlap', is obtained from plots[22] of eigenvalues versus perturbation parameter λ. When two such eigenvalue curves undergo an avoided crossing near some λ, a frequency (an energy difference divided by h) has become nearly zero, and one has an analog of a classical resonance.[26] In a classical resonance, some frequency, i.e., the derivative of H with respect to some action variable, nearly vanishes, reflecting a near commensurability of the frequencies of fundamentals, overtones, or combinations.

In the vicinity of the avoided crossing of two eigenvalue plots each of the two associated wavefunctions is approximately a linear combination of those of the 'uncrossed' curves. When a particular state is simultaneously involved in many such 'overlapping avoided crossings',[27] its wavefunction has a very complicated set of maxima, in contrast to the high regular set depicted in Figure 8. Further, the eigenvalue spacings can no longer be resolved into regular sets of sequences, i.e., the spectrum is now chaotic, even though the eigenvalue differences which constitute the spectrum are near those in the earlier regime where the spacings were more even. The state can be termed quantum mechanically chaotic.[26]

For some systems quantum chaos, described as above, and classical chaos begin at about the same energy,[28,29] i.e., the additional conditions needed for quantum chaos are apparently satisfied, and for others, as in the Henon-Héiles system mentioned earlier, only classical chaos was observed at the perturbation parameter studied.[22]

One approximate method for detecting the onset of quantum chaos was given recently and involves the use of perturbation theory to predict avoided crossings.[29] Plots were made of eigenvalues, calculated perturbatively, versus a perturbation parameter λ. Such plots yield crossings instead of avoided crossings. To obtain the avoided crossings one can use degenerate perturbation theory in the vicinity of each crossing. When the avoided crossings near some λ become extensive at some energy, that energy is the predicted value for the onset of quantum chaos.

We turn finally to the eigenvalue spectrum expected for quantum mechanically 'integrable' systems and for systems near them in some sense.[30] A classical dynamical system of m coordinates is defined as integrable,[31] i.e., as having m good action variables, if there exist m functions F_i in phase space for which the Poisson bracket $\{F_i,F_j\}$ vanishes, with $F_1 = H$. The quantum mechanical analog of this definition is obtained, it has been suggested,[30] using the well-known correspondence[32] between classical and quantum mechanics in which the classical Poisson brackets are replaced by commutators and dynamical variables by Hermetian operators. Thus, one might define an m-coordinate quantum mechanical system as being 'integrable' if for it there exist m operators $\underset{\sim}{F}_i$ with $[\underset{\sim}{F}_i,\underset{\sim}{F}_j] = 0$ and $\underset{\sim}{F}_1 = \underset{\sim}{H}$.[30] Thus, for such systems, a complete set of commuting observables actually exists, whereas for most quantum mechanical systems such a set does not exist, according to this analogy. (In almost all classical systems there do not exist F_i's for which $\{F_i,F_j\} = 0$ and $F_1 = H$ for all initial conditions.)

Examples of these integrable systems are those which permit separation of variables and another[33] for which variables may not yet have been separated but for which the F_i's have been found with $\{F_i,F_j\} = 0$. Indeed, Liouville has apparently shown[34] that given these F_i's with the property that $\{F_i,F_j\} = 0$, and $F_1 = H$, the classical problem can be reduced to quadratures, i.e., is 'integrable'. (Nowadays, this property has been taken as a definition of integrability.[31])

A consequence of this quantum mechanical integrability, i.e., of there being m commuting operators, is that the latter yield a set of m quantum numbers. They, in turn, give rise to a regular series of spectral lines and nodal patterns of wavefunctions. Similar conclusions on the wavefunctions were made earlier from actual pictures of them.[35] The latter picture is further

supported by the semiclassically corresponding trajectory, which fills the same spatial region in which the eigenfunction is concentrated (e.g., cf. Figures 3 and 8). Conjectures on spectra had also been made earlier by analogy with the classical behavior.[36]

In Hamiltonian systems which are close to these integrable systems, i.e., for which the perturbation parameter (or because of scaling the energy) is small enough, it was suggested that qualitatively similar properties of the spectra and wavefunctions (regularly spaced sequences of eigenvalues and more or less regular nodal patterns) might occur.[30] Deviations from these patterns of spectra and nodal surfaces will arrise when avoided crossings (absent in integrable systems) occur. When a quantum state is involved simultaneously in many 'overlapping avoided crossings' it has a 'statistical' (highly delocalized) wavefunction.[27]

We have differentiated between modal and nonmodal energy mixing quasi-periodic states. For some observables it should not matter if instead modal energy mixing has occurred as a result of chaotic behavior. For other observables, those directly connected with the study of sufficiently highly resolved spectra, there would be a difference between the two types of behavior. Some implications of classical and quantum results in this paper for experiments are discussed elsewhere.[7]

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